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(54) ELECTRODE MATERIAL AND METHOD OF MANUFACTURING THE SAME, AND NEGATIVE ELECTRODE FOR NONAQUEOUS SECONDARY BATTERY AND NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous secondary battery of high capacity and superior cycling characteristic, by inhibiting the expansion of an electrode material.

SOLUTION: This electrode material is composed of complex particles including a material including lithium and an alloying element, and a conductive material, a ratio of the material including lithium and the alloying element is not less them 30 mass% and not more than 80 mass% to the total mass of the complex particles, the composite particles have cavities inside thereof, and Vs is at least 35% and not more than 70%, when bulk density of the complex particles is D1 (g/cm3), true density of the complex particles is D2 (g/cm3), and a volumetric population (%) of the cavities of the complex particles is Vs=$(1-1.35 \times D1/D2) \times 100$.
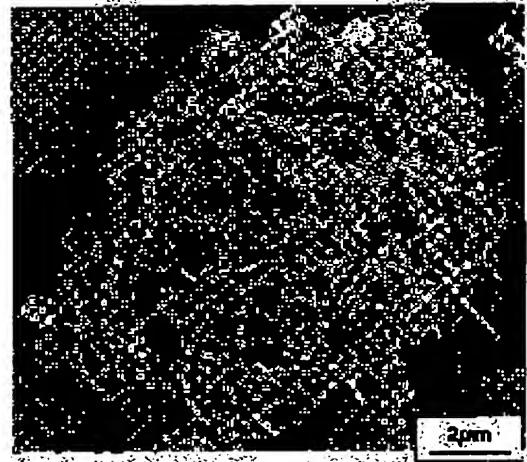
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CLAIMS

[Claim(s)]
[Claim 1] It is the electrode material which consists of a complex particle containing a lithium, the ingredient containing the element which can be alloyed, and a conductive ingredient. The rate of the ingredient containing the element in which said lithium and alloying are possible is below 80 mass % more than 30 mass % to the total mass of said complex particle. Said complex particle has an opening inside. The bulk density of said complex particle D1 (g/cm3), The electrode material with which Vs is characterized by being 70% or less 35% or more when the volume-of-voids pulse duty factor (%) of D2 (g/cm3) and said complex particle is set to Vs= (1-1.35xD1/D2) x100 for the true density of said complex particle.
[Claim 2] The electrode material according to claim 1 whose element in which said lithium and alloying are possible is silicon.
[Claim 3] The electrode material according to claim 1 or 2 whose mean particle diameter the ingredient containing the element in which said lithium and alloying are possible is a particle 2 micrometers or less.
[Claim 4] The electrode material according to claim 1 to 3 said whose conductive ingredient is at least one chosen from the carbon material and the metallic material of fibrous or a coiled form of fibrous or a coiled form.
[Claim 5] The electrode material according to claim 1 to 4 covered with the ingredient with which said complex particle contains carbon.
[Claim 6] The electrode material according to claim 5 with which the ingredient containing said carbon contains at least one chosen from the carbon which calcinates the carbon and the carbon precursor which pyrolyze hydrocarbon system gas in a gaseous phase, and are obtained, and is obtained.
[Claim 7] The manufacture approach of an electrode material including the process which forms a complex particle by mixing and corning the ingredient which is the manufacture approach of an electrode material according to claim 1 to 6, and contains the element in which said lithium and alloying are possible, said conductive ingredient, and resin, and the process which forms an opening in said complex particle by heating said complex particle, making said resin burn or sublimate and removing it.
[Claim 8] The manufacture approach of an electrode material including the process which forms a complex particle by corning by the spray-drying method which is the manufacture approach of an electrode material according to claim 1 to 6, is made to distribute in a solvent the ingredient containing the element in which said lithium and alloying are possible, and said conductive ingredient, considers as mixture, sprays said mixture, and is dried.
[Claim 9] The manufacture approach of an electrode material including the process which forms a complex particle by mixing said complex particle and a different conductive ingredient from said conductive ingredient, and corning further after enforcing the manufacture approach according to claim 7 or 8.
[Claim 10] The manufacture approach of an electrode material including the process which covers said complex particle with the ingredient containing carbon after enforcing the manufacture approach according to claim 7 to 9.
[Claim 11] The negative electrode for nonaqueous rechargeable batteries containing an electrode material according to claim 1 to 6.
[Claim 12] Potential of charge initiation of said negative electrode for nonaqueous rechargeable batteries is set to 1.5V to a lithium metal. To [in the volume of said complex particle after charging quantity of electricity of 1000mAh(s) for the volume of said complex particle at the time of this charge initiation per V1 and 1g of said

complex particles / to V2 and a pan / condition / that / charge / a lithium metal] for said complex particle When the volume of said complex particle after making it discharge to the potential of 1.5V is set to V3 The negative electrode for nonaqueous rechargeable batteries according to claim 11 whose rate of a volumetric shrinkage (%) at the time of the discharge called for by (V2-V3) / (V2-V1) x100 the coefficient of cubical expansion at the time of the charge searched for by (V2-V1) / V1x100 (%) is 68% or less, and is 85% or more.

[Claim 13] The nonaqueous rechargeable battery equipped with the negative electrode for nonaqueous rechargeable batteries according to claim 11 or 12, a positive electrode, and nonaqueous electrolyte.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the negative electrode for nonaqueous rechargeable batteries and nonaqueous rechargeable battery which used the electrode material for the electrode material which can constitute the nonaqueous rechargeable battery which is high capacity and was excellent in the cycle property and its manufacture approach, and a list.
[0002]
[Description of the Prior Art] Since nonaqueous rechargeable batteries are high capacity and high tension, and a high energy consistency, it has a great hope to the development. In this nonaqueous rechargeable battery, the electrolytic solution of the organic solvent system which dissolved the lithium (Li) salt in the organic solvent as the electrolytic solution was used, and Li or Li alloy has been used as a negative-electrode active material. However, when it was made to function as a rechargeable battery, using Li or Li alloy as a negative-electrode active material, in order that the dendrite of Li might generate at the time of charge, since activity was high, the dendrite which lifting-came to be easy of an internal short circuit, and deposited had the problem that safety was missing, with high specific surface area. Furthermore, the coat which the dendrite and solvent in the electrolytic solution reacted, and lacked electronic conduction nature was formed on the front face of a dendrite, the internal resistance of a cell became high, charge-and-discharge effectiveness fell, and there was also a problem that cycle endurance became scarce as the result.
[0003] It replaces with Li or Li alloy, and cycle endurance is improved and it is made to function as a rechargeable battery in the actual condition by using carbon materials, such as amorphous carbon, such as a dope, corks which can be dedoped, and glassy carbon, and a natural or artificial graphite, for Li ion as a negative-electrode ingredient.
[0004] Moreover, like silicon (Si) and tin (Sn), more Li(s) are alloyed, and recently, in order that the semimetal and the metal in which occlusion is possible may attract attention as a negative-electrode ingredient and may enlarge capacity per unit volume, the attempt which uses Si or its compound as a negative-electrode active material is carried out, as high capacity-ization of the rechargeable battery for pocket devices miniaturized and multi-functionalized is desired. For example, the nonaqueous rechargeable battery which used LitSi ($0<=t<=5$) for the patent reference 1 as a negative-electrode active material is indicated.
[0005] Moreover, as advanced technology relevant to this invention, there is patent reference 2 etc., for example.
[0006]
[Patent reference 1] JP,7-29602,A [0007]
[Patent reference 2] JP,2000-272911,A [0008]
[Problem(s) to be Solved by the Invention] However, although the negative-electrode ingredient in which Above Li and alloying are possible is high capacity compared with a carbon material, when charge and discharge are repeated, the negative-electrode ingredient itself repeats and impalpable-powder-izes expansion and contraction, swelling of a negative electrode and unnecessary absorption of the electrolytic solution are caused, and there is a problem that the electrode characteristic deteriorates. The reason is considered as follows.
[0009] For example, Si contains eight Si atoms in the crystallographic unit lattice (a cubic, space group Fd-3m). It converts from the lattice constant of a= 0.5431nm, 0.1602nm of unit-lattice volume is 3, and 0.0199nm (value which **(ed) the unit-lattice volume by Si atomic number in a unit lattice) of volume of one Si atom to occupy

is 3. the potential [negative electrode / which contains Si here] on the basis of Li -- up to 100mV or less -- charging (Li being made to insert) -- although compound Li15Si4 and Li21Si5 containing many Li(s) arise and capacity is equivalent to about 4000 mAh/g, the coefficient of cubical expansion of a negative electrode becomes very large. For example, 83 Si atoms are contained in the unit lattice (a cubic, F-43m of space groups) of Li21Si5. It converts from the lattice constant of a= 1.8750nm, 6.5918nm of unit-lattice volume is 3, and 0.079nm of volume per Si atom is 3. This value is 3.95 times the simple substance Si, and since the volume difference at the time of charge and discharge is very large in this way, a big distortion arises to a negative-electrode particle, and a negative-electrode particle is considered to carry out pulverization. Consequently, space is generated between negative-electrode particles, the electric contact between negative-electrode particles (electronic conduction network) is divided, the part which cannot participate in an electrochemical reaction increases, and it is thought that charge-and-discharge capacity falls.

[0010] Moreover, by the patent reference 2, the lithium secondary battery which used for the negative electrode the complex particle by which Si particle was laid underground into a graphite and noncrystalline carbon was indicated, and the lithium secondary battery excellent in the charge-and-discharge property is realized. Thus, by compound-izing Si particle with a graphite and noncrystalline carbon, expansion of Si can be eased and a cycle property improves. However, by complex particle which discovers the high capacity of about 1000 or more mAh/g, a cycle property does not reach the level suitable for utilization rather than is perfect. Since many Li(s) need to be inserted in Si in order to discover the above high capacity, expansion of Si becomes still larger and this is considered because the structure of a complex particle is destroyed.

[0011] This invention solves the above-mentioned conventional problem, and offers the negative electrode for nonaqueous rechargeable batteries and nonaqueous rechargeable battery which used the electrode material for the electrode material which can constitute the nonaqueous rechargeable battery which is high capacity and was excellent in the cycle property and its manufacture approach, and a list.

[0012]
[Means for Solving the Problem] This invention is an electrode material which consists of a complex particle containing a lithium, the ingredient containing the element which can be alloyed, and a conductive ingredient. The rate of the ingredient containing the element in which said lithium and alloying are possible is below 80 mass % more than 30 mass % to the total mass of said complex particle. Said complex particle has an opening inside. The bulk density of said complex particle D1 (g/cm3), When the volume-of-voids pulse duty factor (%) of D2 (g/cm3) and said complex particle is set to Vs=(1-1.35xD1/D2) x100 for the true density of said complex particle, Vs offers the electrode material which is 70% or less 35% or more.

[0013] Moreover, this invention offers the manufacture approach of an electrode material including the process which forms a complex particle, and the process which forms an opening in said complex particle by heating said complex particle, making said resin burn or sublimate and removing it by mixing and corning the ingredient which is the manufacture approach of the above-mentioned electrode material, and contains the element in which said lithium and alloying are possible, said conductive ingredient, and resin.

[0014] Moreover, this invention is the manufacture approach of the above-mentioned electrode material, distributes in a solvent the ingredient containing the element in which said lithium and alloying are possible, and said conductive ingredient, and is used as mixture, and the manufacture approach of an electrode material including the process which forms a complex particle is offered by corning by the spray-drying method which sprays said mixture and is dried.

[0015] Moreover, this invention offers the negative electrode for nonaqueous rechargeable batteries containing the above-mentioned electrode material.

[0016] Moreover, this invention offers the nonaqueous rechargeable battery equipped with the above-mentioned negative electrode for nonaqueous rechargeable batteries, a positive electrode, and nonaqueous electrolyte.

[0017]
[Embodiment of the Invention] First, the gestalt of operation of the electrode material of this invention is explained. The ingredient as for which one gestalt of the electrode material of this invention contains a lithium and the element which can be alloyed, Are the electrode material which consists of a complex particle containing a conductive ingredient, and the rate of the ingredient containing a lithium and the element which can be alloyed It is below 80 mass % more than 30 mass % to the total mass of a complex particle. When the complex particle has an opening inside and sets [the bulk density of a complex particle] the volume-of-voids

pulse duty factor (%) of D2 (g/cm3) and a complex particle to Vs=(1-1.35xD1/D2) x100 for the true density of D1 (g/cm3) and a complex particle, Vs is 70% or less 35% or more.

[0018] Here, volume-of-voids pulse duty factor Vs=(1-1.35xD1/D2) x100 mean the rate of the volume of voids in the complex particle to the volume of a complex particle. namely, a complex particle -- true -- if it assumes that it is spherical, when the ball will carry out the closest packing in three dimension, it fills up in the shape of a face-centered cubic lattice, and the filling factor (%) becomes as follows.

[0019]
[Equation 1]
$(\sqrt{2}\pi/6) \times 100 = 74.05\%$

[0020] Therefore, bulk density serves as a value reflecting the amount of openings which doubled the opening between the particles accompanying the closest packing, and the opening in a particle. As mentioned above, the opening inside a particle can be expressed with (0.7405.1 / D1)- (1 / D2), and a volume-of-voids pulse duty factor becomes what **(ed) this by the volume (0.7405.1 / D1) of the whole particle. If 1 / 0.7405**1.35, a top type is set to 1-1.35xD1/D2, and a volume-of-voids pulse duty factor (%) will be set to Vs=(1-1.35xD1/D2) x100, applying 100 to this.

[0021] A complex particle will expand greatly that the volume-of-voids pulse duty factor (Vs) of a complex particle is less than 35% at the time of charge. That is, since the clearance which absorbs a part for the expansion in a complex particle is insufficient in case the ingredient containing a lithium and the element which can be alloyed expands with insertion (charge) of Li ion, it is not avoided that a complex particle expands greatly. On the other hand, if Vs exceeds 70%, the production of a complex particle itself becomes difficult, and the clearance in a complex particle increases too much, and since the electronic conduction network of a lithium, the ingredient containing the element which can be alloyed, and a conductive ingredient is hard to be built, charge and discharge will become are hard to be carried out. In addition, the bulk density of the above-mentioned complex particle puts the complex particle of the specified quantity into a container, and asks for it from the bulk density measuring method (JIS R1628) based on the JIS method using a bulk density measuring device. Moreover, it asks for true density from the inert-gas-replacement-type density meter which used gaseous helium.

[0022] Moreover, the content of the ingredient containing a lithium and the element which can be alloyed needs to be in the range of 30 - 80 mass % to the total mass of a complex particle, and its range of 45 - 65 mass % is especially desirable. When realizing high capacity of 1000 mAh/g extent, the utilization factor of the ingredient containing a lithium and the element which can be alloyed becomes high too much, expansion of a complex particle becomes large, and it becomes easy to carry out pulverization of the case of under 30 mass %. Moreover, if 80 mass % is exceeded, since a point of contact with a conductive ingredient will decrease, construction of an electronic conduction network becomes difficult. In addition, it can ask for this content from the quality and quantitative analysis by fluorescence X rays.

[0023] A compound or an element simple substance is sufficient as a metal, semimetal, or a semi-conductor element, and in a crystal, a low crystal, and which an amorphous condition is sufficient as the lithium contained in the above-mentioned complex particle, and the ingredient containing the element which can be alloyed. For example, an oxide, a nitride, etc. may be mentioned as a compound, other alloys, solid solutions, etc. with a metal may be mentioned as a metal, and, otherwise, an intermetallic compound is sufficient. Moreover, that to which B and P were doped in semi-conductor elements, such as Si and germanium, it became the semi-conductor of n mold or p mold, and electric resistance fell greatly may be used. The ingredient containing a lithium and the element which can be alloyed has a desirable globular form, in order to avoid concentration of the internal stress by cubical expansion. Moreover, as an element in which Li and alloying are possible, elements, such as Ag, Au, Zn, Cd, aluminum, Ga, In, Tl, germanium, Pb, Si, Sn, Sb, and Bi, are used preferably. In this, the amount of occlusion of Si of Li is the largest, and it is cheap, and especially since it is satisfactory also in respect of an environment, it is desirable.

[0024] Moreover, as for the ingredient containing the above-mentioned lithium and the element which can be alloyed, it is desirable that mean particle diameter is a particle 2 micrometers or less. It is because it is hard coming to carry out pulverization of the complex particle and cycle endurance can be improved more effectively.

[0025] In this invention, when a complex particle has a predetermined volume-of-voids pulse duty factor, the

opening can be utilized effectively, Li at the time of charge and discharge and the cubical expansion of the ingredient containing the element which can be alloyed can be absorbed, and the cubical expansion of the complex particle itself can be controlled. Therefore, it is desirable that it is at least one chosen from metallic materials, such as a carbon material of fibrous or a coiled form which is easy to form an opening, and copper of fibrous or a coiled form, as a conductive ingredient. Especially, a fibrous carbon material can have the junction of the ingredient which can follow in expansion and contraction of the ingredient containing the above-mentioned lithium and the element which can be alloyed which has the supple shape of thin yarn, and which sake [an element], joins or adjoins effectively, in addition contains the element in which Above Li and alloying are possible since bulk density is large, and many as compared with the acetylene black of the shape of a conventional particle, or an artificial graphite. Furthermore, in order to make it follow in expansion and contraction effectively, as for a fibrous carbon material, what has the elastic force which can be deformed plastically is more desirable.

[0026] As a fibrous carbon material, although especially the fiber length and diameter are not restricted, 1 micrometers or more mean fiber length's 30 micrometers or less are desirable. If it is this within the limits, the electric junction in a complex particle will become good, an electronic conduction network can be built in a complex particle, and a charge-and-discharge property will improve. Moreover, the diameter of a fibrous carbon material has desirable 2 micrometers or less. If it is this within the limits, a fibrous carbon material has sufficient elasticity and can follow in the expansion and contraction accompanying the charge-and-discharge cycle of the ingredient containing a lithium and the element which can be alloyed effectively.

[0027] This fibrous carbon material tends to be ground by strong kneading and strong distributed processing, and it may become impossible to take a fibrous gestalt. Therefore, it is desirable to carry out on the conditions by which a fibrous carbon material cannot be ground easily in the case of compound-izing.

[0028] As a fibrous carbon material, a polyacrylonitrile (PAN) system carbon fiber, a pitch based carbon fiber, a vapor growth carbon fiber, etc. can be used. As conductive ingredients other than a fibrous carbon material, it has high electrical conductivity and high solution retention, and even if the ingredient containing a lithium and the element which can be alloyed contracts, carbon black, such as acetylene black which has the function which can maintain contact, and KETCHIEN black, an artificial graphite, easily graphitized carbon, difficulty graphitized carbon, etc. can use it suitably.

[0029] Moreover, as for the above-mentioned complex particle, being covered with the ingredient which contains carbon further is desirable. It is for controlling expansion of a complex particle effectively and lowering the electric contact resistance between complex particles further. Type section drawing at the time of discharge of the complex particle covered with the ingredient which contains carbon in drawing 3 , and charge is shown. Li and C which is an ingredient containing the element which can be alloyed and which is Si particle and a conductive ingredient, for example -- a predetermined opening -- a coat (enveloping layer) -- a wrap -- expansion of a complex particle can be controlled by things.

[0030] It is desirable to cover with the carbon which pyrolyzes the gas (hydrocarbon system gas) which consists of a compound which contains carbon and hydrogen, such as toluene, especially in a gaseous phase, and is obtained, or the carbon of the difficulty graphitized-carbon (hard carbon) system which calcinates a carbon precursor and is obtained. It is because these carbon is excellent in electronic conduction nature. Moreover, it is more effective if it covers combining the two above-mentioned kinds of carbon.

[0031] The thing of a petroleum system and a coal system can be used as a carbon precursor, for example, acrylic resin, such as a resultant pitch, tar, phenol resin, furan resin, a polyacrylonitrile, and Pori (alpha-halogenation acrylonitrile), polyamidoimide resin, polyamide resin, polyimide resin, etc. can be used. The solvent which dissolves these carbon precursors may be used on the occasion of mixing with a complex particle. As a solvent, hydrocarbons, such as amides, such as various alcohols, such as ketones, such as a tetrahydrofuran and an acetone, a methanol, and ethanol, dimethylformamide, and dimethylacetamide, toluene, a xylene, and benzene, are mentioned, for example. When a solvent is used on the occasion of mixing, a solvent is removed by heating mixture under reduced pressure preferably at the temperature of 50-150 degrees C before baking.

[0032] Moreover, it is desirable to perform the above-mentioned pyrolysis and baking above 700 degrees C, and it is more desirable to carry out above 800 degrees C. It is because conductive good high carbon is obtained that survival of an impurity has little one where processing temperature is higher. When covering a complex

particle with carbon from the above viewpoint, as for the melting point of the ingredient containing a lithium and the element which can be alloyed, it is desirable that it is 700 degrees C or more.

[0033] Next, the gestalt of implementation of the manufacture approach of the electrode material of this invention is explained. One gestalt of the manufacture approach of the complex particle of this invention produces a complex particle by corning a lithium, the ingredient containing the element which can be alloyed, and a conductive ingredient. Then, it mixes with carbon precursors, such as resin, and a carbon precursor can be carbonized or carbon can also cover a complex particle by approaches, such as carrying out a carbon coat with a CVD method (Chemical Vapor Deposition Method). As the granulation approach, rolling granulation, compression granulation, sintering granulation, oscillating granulation, mixing granulation, crack granulation, rolling fluidized bed granulation, the granulation by the spray-drying method, etc. are used suitably.

[0034] The granulation by the spray-drying method is the approach of corning by spraying the slurry which mixed the ingredient and the solvent and drying. Since it is [being grinding and] more efficient to carry out in a solvent for distributing 2 micrometers or less, the granulation according an ingredient particle to the spray-drying method is suitable for making a particle 2 micrometers or less compound-ize. Moreover, control of particle size is also easy the method, and the configuration of the corned particle is also a globular form, and since there are few possibilities that a fiber configuration may be pulverized even if the spray-drying method uses a fibrous conductive ingredient in order to perform neither strong kneading nor strong distributed processing further, it is desirable especially as the granulation approach. As a solvent used for the spray-drying method, it is desirable to use a nonaqueous solvent (solvent which does not contain water). It is because possibility that the front face of the ingredient containing a lithium and the element which can be alloyed will oxidize is high when a drainage system solvent (solvent containing water) is used. Especially as a nonaqueous solvent, alcohols are desirable from a viewpoint of handling nature or the ease of desiccation. Moreover, a bead mill, a ball mill, a wet jet mill, etc. can use it for distribution of a slurry suitably. A polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), etc. can use it for the binder at the time of the granulation which served as the dispersant suitably. The dispersant and binder which remained after granulation can be carbonized by heat-treatment. Moreover, when a rolling granulation, rolling fluidized bed granulation, etc. are performed and the particle is corned with the conductive ingredient of further others after the granulation by the spray-drying method in two steps, especially since an opening can be introduced efficiently and an electronic conduction network can also be built further efficiently, it is desirable.

[0035] The volume-of-voids pulse duty factor in a complex particle is controlling the class of charge of an admixture, mean particle diameter, a mixed rate, granulation conditions, etc., and can attain 35 - 70%. the ratio of the total surface area Ss of the ingredient containing the lithium and the element which can be alloyed especially contained in one complex particle, and the total surface area Sc of a conductive ingredient -- it becomes easy to obtain 35% or more of volume-of-voids pulse duty factor as Sc/Ss is 50 or less [0.5 or more]. Moreover, the size and the amount of an opening of a complex particle can be more effectively controlled by making it contain in the ingredient before corning resin, such as polyethylene (PE) and polystyrene (PS), corning, heating after that, making resin burn or sublimate and removing it.

[0036] Next, the gestalt of operation of the negative electrode for nonaqueous rechargeable batteries of this invention and a nonaqueous rechargeable battery is explained. One gestalt of the negative electrode for nonaqueous rechargeable batteries of this invention is a negative electrode containing the electrode material of this invention explained above.

[0037] Moreover, the negative electrode for nonaqueous rechargeable batteries containing the electrode material of above-mentioned this invention Potential of charge initiation of the negative electrode for nonaqueous rechargeable batteries is set to 1.5V to a lithium metal. To [in the volume of the complex particle after charging quantity of electricity of 1000mAh(s) for the volume of the complex particle at the time of this charge initiation per V1 and 1g of complex particles / to V2 and a pan / condition / that / charge / a lithium metal] for a complex particle to the potential of 1.5V When the volume of the complex particle after making it discharge is set to V3, the coefficient of cubical expansion at the time of the charge searched for by (V2-V1) / V1x100 (%) to 68% or less And the rate of a volumetric shrinkage (%) at the time of the discharge called for by (V2-V3) / (V2-V1) x100 can be made 85% or more.

[0038] The nonaqueous rechargeable battery which is high capacity and was excellent in the cycle property by this can be constituted. That is, when the coefficient of cubical expansion at the time of charge exceeds 68%,

the metallic foil which is a charge collector carries out plasmotomy, and it becomes easy for expansion of the thickness direction of a negative electrode to become large too much, and for distortion etc. to occur in a negative electrode or to produce an adverse effect to cell structure and a component. Moreover, in connection with a charge-and-discharge cycle, possibility that the interior of a complex particle or the electronic conduction network between complex particles will sever becomes high. On the other hand, it is presumed that electric contact into a lithium, the ingredient containing the element which can be alloyed, and a conductive ingredient is inadequate when the rate of a volumetric shrinkage at the time of discharge is less than 85% (i.e., when the complex particle which expanded by charge does not contract at the time of discharge but it is inferior to the reversibility of expansion of the particle in charge and discharge and contraction), and a problem arises in a charge-and-discharge cycle property etc.

[0039] Moreover, as for the complex particle used for the above-mentioned negative electrode for nonaqueous rechargeable batteries, it is desirable that the specific surface area is under 50m2/g. If it is this range, since the binder contained in a negative electrode will not be buried in the surface layer of a complex particle, possibility that the adhesive property of a complex particle and a charge collector will not get worse, but irreversible capacity will increase is low.

[0040] Moreover, one gestalt of the nonaqueous rechargeable battery of this invention is the nonaqueous rechargeable battery equipped with the negative electrode for nonaqueous rechargeable batteries of this invention explained above, a positive electrode, and nonaqueous electrolyte.

[0041] Although especially definition is not carried out, as for the charge approach of the above-mentioned nonaqueous rechargeable battery, it is desirable to carry out by the approach which combined constant current or constant current, and a constant voltage. For example, the method of charging combining the constant-current charge field which charges charge with a fixed current value (I), and the constant-potential charge field which carries out constant-potential charge by the programmed voltage (E) after reaching a programmed voltage (E) is desirable until it reaches a programmed voltage (E). It is because the capacity which the efficient charge of was attained by this and set up by the shortest time amount can be pulled out. In addition, although especially definition is not carried out, as for a charging current value, it is desirable to carry out with two or less 10 mA/cm current density. It is because sufficient capacity will no longer be obtained if this is exceeded.

[0042] Moreover, the cycle property of a nonaqueous rechargeable battery may improve by restricting the amount of Li(s) by which occlusion is carried out to the ingredient containing a lithium and the element which can be alloyed. For example, although Si is charged and an alloy (LixSi) with Li is formed, it is desirable that it is the range of $x<=2.625$, in exceeding x= 2.625 (Li21Si8), an expansion coefficient becomes large, and the result that a cycle property falls is obtained.

[0043] the complex particle of this invention -- a simple substance -- a binder -- mixing -- the object for negative electrodes -- although it can consider as a mixture (mixture of a negative-electrode component), the electrical conducting material further for negative electrodes may be introduced. the object for negative electrodes -- the electrical conducting material for negative electrodes at the time of producing a mixture Although there will be especially no limit if it is the electronic conduction nature ingredient which does not cause a chemical change in the constituted nonaqueous rechargeable battery Usually, natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, One sort or these can be mixed and conductive polymers, such as carbon black, such as acetylene black and KETCHIEN black, a carbon fiber, a metal powder (powder, such as copper, nickel, aluminum, and silver) and a metal fiber, or a polyphenylene derivative, can be used.

[0044] As a binder used for the above-mentioned negative electrode, for example Starch, polyvinyl alcohol, A carboxymethyl cellulose, hydroxypropylcellulose, a regenerated cellulose, Diacetyl cellulose, polyvinyl chloride, a polyvinyl pyrrolidone, Polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, Polypropylene, an ethylene-propylene-diene terpolymer (EPDM), One sort, such as polymers which have polysaccharide, such as sulfonation EPDM, styrene butadiene rubber, butadiene rubber, polybutadiene, a fluororubber, and polyethylene oxide, thermoplastics, and rubber elasticity, and these conversion objects, or two sorts or more can be mixed and used.

[0045] A positive-electrode ingredient, an electrical conducting material, a binder, etc. are contained in the above-mentioned positive electrode. Although various kinds of things can be used without being limited especially as this positive-electrode ingredient Especially LixCoO2, LixNiO2, LixMnO2, LixCoyNi1-yO2,

LixCoyM1-yOz, LixNi1-yMyOz, LixMn 2O4, LixMn2-yMyO4 (M) It is at least one sort and 0<=x<=1.1 among Mg, Mn, Fe, Co, nickel, Cu, Zn, aluminum, and Cr. 0< y<1.0 Li content transition-metals oxides, such as 2.0<=z<=2.2, are used suitably.

[0046] If it is the electronic conduction nature ingredient which does not cause a chemical change as an electrical conducting material for positive electrodes in the charge and discharge potential of the positive-electrode ingredient to be used, especially the class will not be restricted. For example, conductive fiber, such as carbon black, such as graphite, such as a natural graphite and an artificial graphite, or acetylene black, KETCHIEN black, channel black, furnace black, lamp black, and thermal black, or a carbon fiber, and a metal fiber, can be used for independence or these, mixing. In these electrical conducting materials, an artificial graphite, acetylene black, and especially KETCHIEN black are desirable.

[0047] As a binder for positive electrodes, for example Polyethylene, polypropylene, Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), Styrene butadiene rubber, a tetrafluoroethylene-hexafluoro ethylene copolymer, A tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer, a vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-chlorotrifluoroethylene copolymer, an ethylene-tetrafluoroethylene copolymer, etc. -- it can be used -- these ingredients -- independence -- or it can mix and use. Moreover, the more desirable ingredients in these ingredients are PVDF and PTFE.

[0048] Although either the liquefied electrolyte generally called the electrolytic solution a gel polymer electrolyte or a solid electrolyte can be used as nonaqueous electrolyte of lithium ion conductivity used for the nonaqueous rechargeable battery of this invention, a liquefied electrolyte, a gel polymer electrolyte, etc. are desirable.

[0049] The liquefied electrolyte consists of an organic solvent and a Li salt which dissolves in the organic solvent. As an organic solvent, propylene carbonate, ethylene carbonate, Butylene carbonate, dimethyl carbonate, diethyl carbonate, Methylethyl carbonate, gamma-butyrolactone, 1, 2-dimethoxyethane, A tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1, 3-dioxolane, a formamide, dimethylformamide, dioxolane, An acetonitrile, nitromethane, methyl formate, methyl acetate, phosphoric acid triester, Trimethoxy methane, a dioxolane derivative, a sulfolane, 3-methyl-2-oxazolidinone, The solvent which mixed at least one or more sorts of aprotic organic solvents, such as propylene carbonate derivative, tetrahydrofuran derivative, diethylether, 1, and 3-propane sultone, can be used. Moreover, as a Li salt dissolved in the organic solvent, one or more sorts, such as LiClO4, LiBF6, LiPF6, LiCF3SO3, LiCF3Cs O2, LiAsF6, and LiSbF6, LiB10Cl10, low-grade aliphatic carboxylic acid Li and LiAlCl4, LiCl, LiBr, LiI, the chloro borane Li, and the 4 phenyl boric acid Li, can be used, for example. Especially, the liquefied electrolyte which made the mixed solvent with ethylene carbonate or propylene carbonate, 1, 2-dimethoxyethane and diethyl carbonate, methylethyl carbonate, etc. contain LiClO4, LiBF6, LiPF6, LiCF3SO3, etc. is desirable. although especially the amount that pours in these liquefied electrolytes into a cell is not limited -- the amount of an active material, and the size of a cell -- **** for initial complements -- things are made. Although especially the concentration of Li salt in this liquefied electrolyte is not limited, 0.2-3.0 mols per 1l. of liquefied electrolytes are desirable.

[0050] Moreover, a gel polymer electrolyte is equivalent to what gelled the above-mentioned liquefied electrolyte with the gelling agent. As the gelling agent, for example Straight chain-like polymers or those copolymers, such as polyethylene oxide and the poly acrylic nitril, Or the polyfunctional monomer polymer-ized by the exposure of activity beams of light, such as ultraviolet rays and an electron ray, For example, pentaerythritol tetraacrylate, ditrimethylolpropanetetraacrylate, Ethoxylation pentaerythritol tetraacrylate, dipentaerythritol hydroxy pentaacrylate, The acrylate of four or more organic functions, such as dipentaerythritol hexaacrylate, and the above-mentioned acrylate, the same methacrylate of four or more organic functions, etc. are used. However, even when using the above-mentioned monomer, the monomer itself remains as it is, and it does not become a gelling agent, but the polymer which polymer-ized them acts as a gelling agent.

[0051] When making a liquefied electrolyte gel using polyfunctional monomer as mentioned above, if required, as a polymerization initiator, for example, benzoyls, benzoin alkyl ether, benzophenones, benzoyl phenyl phosphoretted hydrogen oxide, acetophenones, thioxan tons, and anthraquinone can be used, and alkylamines, amino ester, etc. can be further used as a sensitizer of a polymerization initiator.

[0052] The large-sized things used for an electric vehicle besides being a coin mold, a carbon button mold, a

sheet mold, a laminating mold, cylindrical, flat, a square shape, etc. as a configuration of the nonaqueous rechargeable battery of this invention may be any.

[0053]

[Example] Hereafter, an example explains this invention in more detail. However, this invention is not limited to these examples.

[0054] (Example 1) Fibrous carbon (CF: carbon fiber) with a diameter of 0.2 micrometers and a graphite with a mean particle diameter of 2 micrometers were mixed with Si powder with a mean particle diameter of 1 micrometer with the mass ratio by 5 micrometers of mean fiber length at the compounding ratio of Si:CF:graphite =60:30:10, and these were corned using the tumbling granulator of a churning type. Consequently, the complex particle with a mean particle diameter of 10 micrometers was obtained. The true density (D2) of the complex particle was 3, and 2.20g (D1)/cm of bulk density was 0.8 g/cm3. Therefore, the volume-of-voids pulse duty factor Vs of this complex particle was able to be found with 51% from the formula of Vs=(1-1.35xD1/D2) x100.

[0055] As opposed to the obtained complex particle 90 mass section as an electrical conducting material for negative electrodes Next, the carbon powder 5 mass section, The PVDF5 mass section was mixed as a binder, the dehydration N-methyl pyrrolidone was made to distribute these, the slurry was produced, and it applied on the negative-electrode charge collector which consists of copper foil, it dried, and after rolling out, it cut off to disc-like [with a diameter of 16mm], this was dried under vacuum for 24 hours, and it considered as the negative electrode.

[0056] About the complex particle obtained above, the property as an electrode material of the negative electrode for nonaqueous rechargeable batteries was examined by the following approach.

[0057] The coin mold model cell was produced combining the above-mentioned negative electrode and the metal Li of a counter electrode. What carried out 1 mol/L dissolution of the 6 fluoride [phosphoric-acid] lithium was used for the mixed solvent (mixed volume ratio 1:1) of propylene carbonate and dimethyl carbonate at the electrolytic solution. After discharging until the potential of a negative electrode was set to 1.5V on lithium metal criteria, some model cells were disassembled and it asked for the volume V1 of the complex particle at the time of charge initiation by the below-mentioned approach. Subsequently, the complex particle of a negative electrode was charged for the remaining cell with quantity of electricity of 1000mAh(s) perg, and it asked for the volume V2 of a complex particle by the same approach from some cells in this. Furthermore, the remaining cells were made to discharge until the potential of a negative electrode was set to 1.5V on lithium metal criteria, and it asked for the volume V3 of a complex particle by the approach that it is the same after discharge termination. It asked for the coefficient of cubical expansion at the time of charge [(V2-V1) /V1x100], and the rate of a volumetric shrinkage at the time of discharge [(V2-V3) /(V2-V1) x100] from this result. Consequently, the coefficient of cubical expansion at the time of charge was 65%, and the rate of a volumetric shrinkage at the time of discharge was 85%.

[0058] It asked for the volume of the above-mentioned complex particle by the following approach. After dimethyl carbonate washed the negative electrode to measure under the argon ambient atmosphere, even the scanning electron microscope (SEM) was conveyed in the airtight condition, without touching atmospheric air, and it asked for the particle size of 100 particles of arbitration from the SEM photograph, and it asked for the volume, having assumed the configuration of a complex particle to be spherical. And average particle volume of 100 pieces was made into the volume of the complex particle for which it asks.

[0059] On the other hand, the cycle property of the coin mold model cell using the above-mentioned complex particle was investigated. The charge-and-discharge approach of a cell was performed as follows. Charge charged by the constant voltage after making current density into 0.5 mA/cm2, charging by constant current and a charge electrical potential difference's amounting to 120mV until it became the current density of 1/10. Discharge was performed by the constant current of current density 0.5 mA/cm2, and discharge final voltage was set to 1.5V.

[0060] Consequently, the discharge capacity of a two-cycle eye was 1100mAh(s) per 1g of complex particles, and the capacity retention [(discharge capacity of the discharge capacity / two-cycle eye of 50 cycle eye) x100] of 50 cycle eye was 70%.

[0061] (Example 2) CF with a diameter of 0.2 micrometers and a graphite with a mean particle diameter of 2 micrometers were mixed with Si powder with a mean particle diameter of 1 micrometer with the mass ratio by 5

micrometers of mean fiber length at the compounding ratio of Si:CF:graphite =60:30:10, and these were corned using the tumbling granulator of a churning type. Consequently, the complex particle with a mean particle diameter of 10 micrometers was obtained. Thus, the SEM photograph of the produced complex particle is shown in <u>drawing 1</u> .

[0062] Then, the CVD method covered the complex particle by 1000 degrees C with carbon by making benzene into the source of carbon. The covered carbon content was calculated from mass change of the complex particle before and behind a coat. The presentation of the complex particle was Si:CF:graphite:CVD carbon =56:28:9:7 in the mass ratio. The true density of the obtained complex particle was 2.20 g/cm3, and bulk density was 0.85 g/cm3. Therefore, the volume-of-voids pulse duty factor Vs of this complex particle was able to be found with 48% from the above-mentioned formula. Next, when the negative electrode was produced like the example 1, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 50%, and the rate of a volumetric shrinkage at the time of discharge was 92%.

[0063] Moreover, as a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1000mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 85%.

[0064] (Example 3) The complex particle was produced like the example 2 except having used CF with a diameter of 0.2 micrometers and a graphite with a mean particle diameter of 2 micrometers with the compounding ratio of Si:CF:graphite =60:30:10 with the mass ratio by Si particle with a mean particle diameter of 2 micrometers and 5 micrometers of mean fiber length. Si content of the obtained complex particle was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 0.98 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 40%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 62%, and the rate of a volumetric shrinkage at the time of discharge was 88%.

[0065] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 950mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 75%.

[0066] (Example 4) The complex particle was produced like the example 2 using the same raw material as an example 1 except having set the compounding ratio to Si:CF:graphite =40:35:25 with the mass ratio. Si content of the obtained complex particle was 37 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 0.81 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 50%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 50%, and the rate of a volumetric shrinkage at the time of discharge was 92%.

[0067] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 700mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 95%.

[0068] (Example 5) The complex particle was produced like the example 2 using the same raw material as an example 1 except having set the compounding ratio to Si:CF:graphite =75:15:10 with the mass ratio. Si content of the obtained complex particle was 70 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.25 g/cm3, and bulk density was 1.0 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 40%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 55%, and the rate of a volumetric shrinkage at the time of discharge was 85%.

[0069] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1250mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 73%.

[0070] (Example 6) The complex particle was produced like the example 2 except having used CF with a diameter of 0.1 micrometers and a graphite with a mean particle diameter of 2 micrometers with the compounding ratio of Si:CF:graphite =60:30:10 with the mass ratio by Si particle with a mean particle diameter of 1 micrometer and 10 micrometers of mean fiber length. Si content of the obtained complex particle was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 0.73 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 55%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 45%, and the rate of a volumetric shrinkage at the time of discharge was 92%.

[0071] As a result of the cycle trial performed like the example 1, the discharge capacity of a two-cycle eye was 1050mAh(s) per 1g of complex particles, and the capacity retention of the electrode of 50 cycle eye was 87%.

[0072] (Example 7) The complex particle was produced like the example 2 except having used CF with a diameter of 0.2 micrometers with the compounding ratio of Si:CF=60:40 with the mass ratio by Si particle with a mean particle diameter of 1 micrometer and 10 micrometers of mean fiber length. After coating the obtained complex particle with a coal-tar pitch, it calcinated at 1300 degrees C and the front face of a complex particle was covered with hard carbon.

[0073] Si content of the complex particle obtained eventually was 52 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.10 g/cm3, and bulk density was 0.86 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 45%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 35%, and the rate of a volumetric shrinkage at the time of discharge was 95%.

[0074] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 950mAh(s) per 1g of complex particles, and the capacity retention of the electrode of 50 cycle eye was 88%.

[0075] (Example 8) The polystyrene particle (PS) of 0.2 micrometers of mean diameters is further added to the same raw material as an example 1, and it is a Si:CF:graphite at a mass ratio :P The complex particle was produced like the example 2 except having used with the compounding ratio of S= 30:15:5:50. In order to burn or sublimate used PS at the time of CVD processing, a new opening is formed in a particle. Si content of the complex particle obtained eventually was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 0.73 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 55%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 48%, and the rate of a volumetric shrinkage at the time of discharge was 90%.

[0076] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 920mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 85%.

[0077] (Example 9) The complex particle was produced like the example 2 except having used CF with a diameter of 0.2 micrometers and KETCHIEN black (KB) with a mean particle diameter of 0.05 micrometers with the compounding ratio of Si:CF:KB=60:30:10 with the mass ratio by Si particle with a mean particle diameter of 0.2 micrometers and 5 micrometers of mean fiber length. Si content of the obtained complex particle was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.10 g/cm3, and bulk density was 0.68 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 56%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 50%, and the rate of a volumetric shrinkage at the time of discharge was 95%.

[0078] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1000mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 87%.

[0079] (Example 10) CF with a diameter of 0.2 micrometers, KB with a mean particle diameter of 0.05 micrometers, and the polyvinyl pyrrolidone (PVP) as a dispersant were mixed with Si powder with a mean particle diameter of 0.2 micrometers in ethanol with the mass ratio by 5 micrometers of mean fiber length at the compounding ratio of Si:CF:KB:PVP=60:30:10:4. The slurry which carried out distributed mixing of this mixture with the wet jet mill, and was obtained after that was corned by the spray-drying method. Consequently, the granulation object with a mean particle diameter of 10 micrometers was acquired. Then, the CVD method covered the complex particle by 1000 degrees C with carbon by making toluene into the source of carbon. The covered carbon content was calculated from mass change of the complex particle before and behind a coat. The presentation of the complex particle was Si:CF:KB:CVD carbon =50:25:8:17 in the mass ratio. The true density of the obtained complex particle was 2.10 g/cm3, and bulk density was 0.68 g/cm3. Therefore, the volume-of-voids pulse duty factor was able to be found with 58%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 48%, and the rate of a volumetric shrinkage at the time of discharge was 95%.

[0080] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1000mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 90%.

[0081] (Example 11) Si powder with a mean particle diameter of 0.2 micrometers, KB with a mean particle diameter of 0.05 micrometers, and PVP as a dispersant were mixed in ethanol with the compounding ratio of Si:KB:PVP=70:30:3 with the mass ratio. The slurry which carried out distributed mixing of this mixture with

the wet jet mill, and was obtained after that was corned by the spray-drying method. Consequently, the granulation object with a mean particle diameter of 3 micrometers was acquired. CF with a diameter of 0.2 micrometers was mixed with the acquired granulation object (Si/KB granulation object) with the mass ratio by 5 micrometers of mean fiber length at the compounding ratio of Si/KB granulation object:CF=85:15, and the mixture was corned with the rolling gas flow method. Consequently, the complex particle with a mean particle diameter of 15 micrometers was obtained. Then, the CVD method covered the complex particle by 1000 degrees C with carbon by making toluene into the source of carbon. The covered carbon content was calculated from mass change of the complex particle before and behind a coat. The presentation of the complex particle was Si:CF:KB:CVD carbon =50:10:25:15 in the mass ratio. The true density of the obtained complex particle was 2.10 g/cm3, and bulk density was 0.65 g/cm3. Therefore, the volume-of-voids pulse duty factor was able to be found with 60%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 47%, and the rate of a volumetric shrinkage at the time of discharge was 95%.

[0082] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1000 mAh per 1g of complex particles, and the capacity retention of 50 cycle eye was 92%.

[0083] (Example 12) Si powder with a mean particle diameter of 1.0 micrometers, KB with a mean particle diameter of 0.05 micrometers, and PVP of a dispersant were mixed in ethanol with the compounding ratio of Si:KB:PVP=70:30:3 with the mass ratio. The slurry which carried out distributed mixing of this mixture with the wet jet mill, and was obtained after that was corned by the spray-drying method. Consequently, the granulation object with a mean particle diameter of 5 micrometers was acquired. Then, the CVD method covered the granulation object by 1000 degrees C with carbon by making toluene into the source of carbon. After coating the obtained complex particle with a coal-tar pitch further, it calcinated at 1300 degrees C and the front face of a complex particle was covered with hard carbon.

[0084] Thus, the SEM photograph of the produced complex particle is shown in drawing 2 . Si content of the complex particle obtained eventually was 47 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.10 g/cm3, and bulk density was 0.78 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 50%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 40%, and the rate of a volumetric shrinkage at the time of discharge was 95%.

[0085] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 920mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 93%.

[0086] (Example 13) Si powder with a mean particle diameter of 1.0 micrometers, KB with a mean particle diameter of 0.05 micrometers, and PVP of a dispersant were mixed in ethanol with the compounding ratio of Si:KB:PVP=60:40:4 with the mass ratio. The slurry which carried out distributed mixing of this mixture with the wet jet mill, and was obtained after that was corned by the spray-drying method. Consequently, the granulation object with a mean particle diameter of 5 micrometers was acquired. Then, the granulation object was calcinated without the source of carbon at 1000 degrees C. Si content of the complex particle obtained eventually was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.10 g/cm3, and bulk density was 0.75 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 52%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 55%, and the rate of a volumetric shrinkage at the time of discharge was 85%.

[0087] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1050 mAh per 1g of complex particles, and the capacity retention of the electrode of 50 cycle eye was 80%.

[0088] (Example 14) Si/Si2nickel complex powder with a mean particle diameter of 1.0 micrometers, KB with a mean particle diameter of 0.05 micrometers, and PVP of a dispersant were mixed in ethanol with the compounding ratio of Si:KB:PVP=85:15:1 with the mass ratio. The slurry which carried out distributed mixing of this mixture with the wet jet mill, and was obtained after that was corned by the spray-drying method. Consequently, the granulation object with a mean particle diameter of 7 micrometers was acquired. Then, the CVD method covered the granulation object by 850 degrees C with carbon by making toluene into the source of carbon. Si content of the complex particle obtained eventually was 40 mass % to the total mass of a complex particle, and the true density of the complex particle was 3.10 g/cm3, and bulk density was 1.15 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 50%.

Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 40%, and the rate of a volumetric shrinkage at the time of discharge was 93%.

[0089] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 800mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 95%.

[0090] (Example 1 of a comparison) The complex particle was produced like the example 1 except having used Si powder with a mean particle diameter of 1 micrometer and a graphite with a mean particle diameter of 2 micrometers with the compounding ratio of Si:graphite =60:40 with the mass ratio. Si content of the obtained complex particle was 56 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 1.14 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 30%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 100%, and the rate of a volumetric shrinkage at the time of discharge was 77%.

[0091] Although the discharge capacity of a two-cycle eye was 840mAh(s) per 1g of complex particles as a result of performing a cycle trial like an example 1, the capacity retention of 50 cycle eye is 40%, and sharp capacity lowering was accepted.

[0092] (Example 2 of a comparison) The complex particle was produced like the example 1 except having used Si powder with a mean particle diameter of 1 micrometer and a graphite with a mean particle diameter of 2 micrometers with the compounding ratio of Si:graphite =90:10 with the mass ratio. Si content of the obtained complex particle was 84 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 1.10 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 32%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 110%, and the rate of a volumetric shrinkage at the time of discharge was 70%.

[0093] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 1400mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 10%.

[0094] (Example 3 of a comparison) The complex particle was produced like the example 1 except having used Si powder with a mean particle diameter of 1 micrometer and a graphite with a mean particle diameter of 2 micrometers with the compounding ratio of Si:graphite =25:75 with the mass ratio. Si content of the obtained complex particle was 20 mass % to the total mass of a complex particle, and the true density of the complex particle was 2.20 g/cm3, and bulk density was 1.17 g/cm3. Therefore, the volume-of-voids pulse duty factor of this complex particle was able to be found with 28%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 is 75%, and the rate of a volumetric shrinkage at the time of discharge was able to be found with 83%.

[0095] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 500mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 50%.

[0096] (Example 1 of reference) The tetramethoxy silane (TMOS) was dissolved in the tetrahydrofuran (THF) solution of a coal-tar pitch. Stirring and mixing of were done having added the graphite with a mean particle diameter of 5 micrometers in this solution, and flowing back in it. each compounding ratio -- a mass ratio -- THF:coal-tar pitch: -- TMOS: -- it is graphite =10:1:1:3. Subsequently, the vacuum drying of the THF was carried out and it was removed. A coal-tar pitch and TMOS were decomposed and carbonized for the obtained powder at 1000 degrees C among the nitrogen air current, and the complex particle which consists of the graphite and amorphous carbon containing silicon was obtained. Si content of this complex particle was 6 mass % to the total mass of a complex particle, and the volume-of-voids pulse duty factor of that complex particle was 12%. Moreover, the coefficient of cubical expansion at the time of the charge measured like the example 1 was 30%, and the rate of a volumetric shrinkage at the time of discharge was 80%.

[0097] As a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 400mAh(s) per 1g of complex particles, and the capacity retention of 50 cycle eye was 70%.

[0098] (Example 2 of reference) By Si particle with a mean particle diameter of 2 micrometers and 5 micrometers of mean fiber length, it mixed with the mortar with the mass ratio at the compounding ratio of Si:CF=60:40, and CF with a diameter of 0.2 micrometers was used as the electrode material. This electrode material is [that Si and CF are only only mixed and], and complex was not formed. The negative electrode was produced like the example 1 using this electrode material.

[0099] Moreover, as a result of performing a cycle trial like an example 1, the discharge capacity of a two-cycle eye was 650mAh(s) per 1g of complex particles, and most discharge capacity of 50 cycle eye was 0 mAh/g.

[0100] The above result was shown in a table 1.

[0101]

[A table 1]

	空隙体積占有率Vs（％）	充電時の体積膨張率（％）	放電時の体積収縮率（％）	2サイクル目の放電容量（mAh／g）	50サイクル目容量保持率（％）
実施例1	51	65	85	1100	70
実施例2	48	50	92	1000	85
実施例3	40	62	88	950	75
実施例4	50	50	92	700	95
実施例5	40	55	85	1250	73
実施例6	55	45	92	1050	87
実施例7	45	35	95	950	88
実施例8	55	48	90	920	85
実施例9	56	50	95	1000	87
実施例10	58	48	95	1000	90
実施例11	60	47	95	1000	92
実施例12	50	40	95	920	93
実施例13	52	55	85	1050	80
実施例14	50	40	93	800	95
比較例1	30	100	77	840	40
比較例2	32	110	70	1400	10
比較例3	28	75	83	500	50
参考例1	12	30	80	400	70
参考例2	—	—	—	650	0

[0102] The complex particle of examples 1-14 has little expansion of the particle at the time of charge, and it turns out that it can contract reversibly at the time of discharge so that clearly from a table 1. Moreover, a big discharge capacity was shown, and even if it repeated the charge-and-discharge cycle, capacity lowering was excellent also in the cycle property few. On the other hand, the examples 1-3 of a comparison with a small volume-of-voids pulse duty factor had the large expansion at the time of charge, and were inferior to reversibility, and the capacity retention after a charge-and-discharge cycle also became remarkably low.

[0103] In addition, the example 1 of reference is an example modeled after the patent reference 2, and the example 2 of reference is an example in which the complex particle is not made to form.

[0104]

[Effect of the Invention] As explained above, this invention can constitute the nonaqueous rechargeable battery which is high capacity and was excellent in the cycle property by suppressing expansion of an electrode material.

[Translation done.]

DRAWINGS

[Drawing 1]

2μm

[Drawing 2]

1.5μm

[Drawing 3]

放電　　被覆層　　充電

C
Si
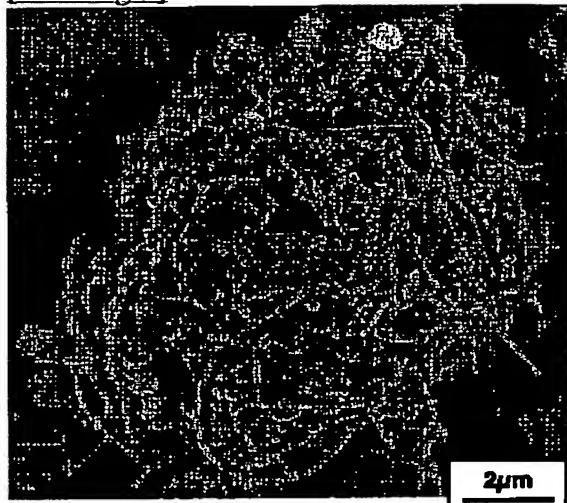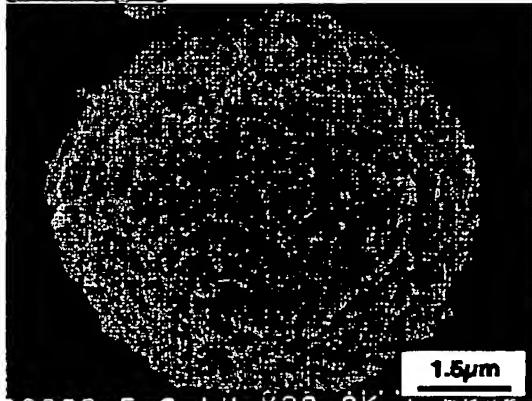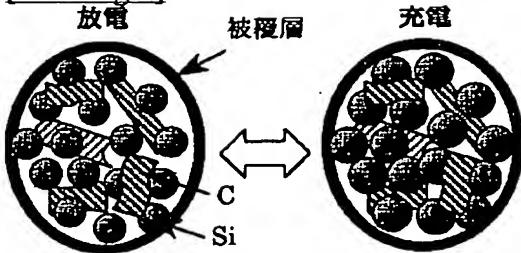
[Translation done.]

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審査請求 有 請求項の数13 OL （全 12 頁）

(54)【発明の名称】電極材料およびその製造方法、並びに非水二次電池用負極および非水二次電池

(57)【要約】

【課題】 電極材料の膨張を抑えることにより、高容量でかつサイクル特性に優れた非水二次電池を提供する。

【解決手段】 リチウムと合金化可能な元素を含む材料と、導電性材料とを含む複合体粒子からなる電極材料であって、リチウムと合金化可能な元素を含む材料の割合が、複合体粒子の全質量に対して３０質量％以上８０質量％以下であり、複合体粒子が、内部に空隙を有し、複合体粒子の嵩密度をD1（g／cm³)、複合体粒子の真密度をD2（g／cm³)、複合体粒子の空隙体積占有率（％）をVs＝（1－1.35×D1／D2)×100とした場合、Vsが３５％以上７０％以下である電極材料とする。

2μm
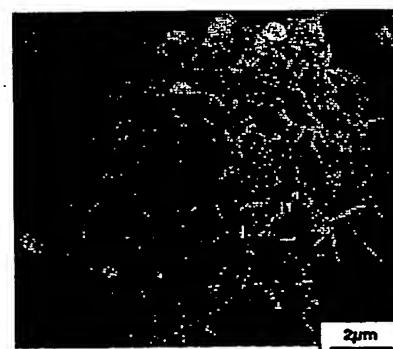
【特許請求の範囲】

【請求項１】　リチウムと合金化可能な元素を含む材料と、導電性材料とを含む複合体粒子からなる電極材料であって、

前記リチウムと合金化可能な元素を含む材料の割合が、前記複合体粒子の全質量に対して３０質量％以上８０質量％以下であり、

前記複合体粒子が、内部に空隙を有し、

前記複合体粒子の嵩密度をＤ１（ｇ／ｃｍ³）、前記複合体粒子の真密度をＤ２（ｇ／ｃｍ³）、前記複合体粒子の空隙体積占有率（％）をＶｓ＝（１－１．３５×Ｄ１／Ｄ２）×１００とした場合、Ｖｓが３５％以上７０％以下であることを特徴とする電極材料。

【請求項２】　前記リチウムと合金化可能な元素が、ケイ素である請求項１に記載の電極材料。

【請求項３】　前記リチウムと合金化可能な元素を含む材料が、平均粒径が２μｍ以下の粒子である請求項１または２に記載の電極材料。

【請求項４】　前記導電性材料が、繊維状またはコイル状の炭素材料および繊維状またはコイル状の金属材料から選ばれる少なくとも一つである請求項１～３のいずれかに記載の電極材料。

【請求項５】　前記複合体粒子が、炭素を含む材料によって被覆されている請求項１～４のいずれかに記載の電極材料。

【請求項６】　前記炭素を含む材料が、炭化水素系ガスを気相中で熱分解して得られる炭素および炭素前駆体を焼成して得られる炭素から選ばれる少なくとも一つを含む請求項５に記載の電極材料。

【請求項７】　請求項１～６のいずれかに記載の電極材料の製造方法であって、

前記リチウムと合金化可能な元素を含む材料と、前記導電性材料と、樹脂とを混合して造粒することにより複合体粒子を形成する工程と、

前記複合体粒子を加熱して前記樹脂を燃焼または昇華させて除去することにより、前記複合体粒子内に空隙を形成する工程とを含む電極材料の製造方法。

【請求項８】　請求項１～６のいずれかに記載の電極材料の製造方法であって、

前記リチウムと合金化可能な元素を含む材料と、前記導電性材料とを溶媒中で分散させて混合物とし、前記混合物を噴霧して乾燥するスプレードライ法により造粒することにより複合体粒子を形成する工程を含む電極材料の製造方法。

【請求項９】　請求項７または８に記載の製造方法を実施した後に、前記複合体粒子と、前記導電性材料とは異なる導電性材料とを混合してさらに造粒することにより複合体粒子を形成する工程を含む電極材料の製造方法。

【請求項１０】　請求項７～９のいずれかに記載の製造方法を実施した後に、前記複合体粒子を、炭素を含む材料により被覆する工程を含む電極材料の製造方法。

【請求項１１】　請求項１～６のいずれかに記載の電極材料を含む非水二次電池用負極。

【請求項１２】　前記非水二次電池用負極の充電開始の電位をリチウム金属に対して１．５Ｖとし、この充電開始時の前記複合体粒子の体積をＶ１、前記複合体粒子１ｇ当たり１０００ｍＡｈの電気量の充電を行った後の前記複合体粒子の体積をＶ２、さらにその充電状態から前記複合体粒子をリチウム金属に対して１．５Ｖの電位まで放電させた後の前記複合体粒子の体積をＶ３とした場合に、（Ｖ２－Ｖ１）／Ｖ１×１００で求められる充電時の体積膨張率（％）が６８％以下であり、かつ、（Ｖ２－Ｖ３）／（Ｖ２－Ｖ１）×１００で求められる放電時の体積収縮率（％）が８５％以上である請求項１１に記載の非水二次電池用負極。

【請求項１３】　請求項１１または１２に記載の非水二次電池用負極と、正極と、非水電解質とを備えた非水二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、高容量でかつサイクル特性に優れた非水二次電池を構成することのできる電極材料およびその製造方法、並びにその電極材料を用いた非水二次電池用負極および非水二次電池に関する。

【０００２】

【従来の技術】非水二次電池は高容量かつ高電圧、高エネルギー密度であることから、その発展に対して大きな期待が寄せられている。この非水二次電池では、電解液として有機溶媒にリチウム（Ｌｉ）塩を溶解させた有機溶媒系の電解液が用いられ、負極活物質としてＬｉまたはＬｉ合金が用いられてきた。しかし、負極活物質としてＬｉまたはＬｉ合金を用いて二次電池として機能させた場合、充電時にＬｉのデンドライトが生成するために内部短絡を起こしやすくなり、また、析出したデンドライトは高比表面積で活性が高いため安全性に欠けるという問題があった。さらに、そのデンドライトと電解液中の溶媒とが反応して電子伝導性を欠いた被膜がデンドライトの表面上に形成されて電池の内部抵抗が高くなり、充放電効率が低下し、その結果としてサイクル耐久性が乏しくなるという問題もあった。

【０００３】現状では、ＬｉやＬｉ合金に代えて、Ｌｉイオンをドープ・脱ドープすることが可能なコークスやガラス状炭素などの非晶質炭素、天然または人造の黒鉛などの炭素材料を負極材料として用いることによってサイクル耐久性を改善し、二次電池として機能させている。

【０００４】また最近では、小型化および多機能化した携帯機器用二次電池の高容量化が望まれるにつれて、ケイ素（Ｓｉ）や錫（Ｓｎ）などのように、より多くのＬｉを合金化して吸蔵可能な半金属および金属が負極材料

として注目を集めており、単位体積当たりの容量を大きくするため、Ｓｉまたはその化合物を負極活物質とする試みがされている。例えば、特許文献１には、Ｌｉ$_t$Ｓｉ（０≦ｔ≦５）を負極活物質として用いた非水二次電池が開示されている。

【０００５】また、本発明に関連する先行技術としては、例えば特許文献２などがある。

【０００６】

【特許文献１】特開平７－２９６０２号公報

【０００７】

【特許文献２】特開２０００－２７２９１１号公報

【０００８】

【発明が解決しようとする課題】しかし、上記Ｌｉと合金化可能な負極材料は炭素材料に比べて高容量であるが、充放電を繰り返すと、負極材料自体が膨張・収縮を繰り返して微粉末化し、負極の膨潤や電解液の不必要な吸収を引き起こし、電極特性が劣化するという問題がある。その理由は以下のように考えられる。

【０００９】例えば、Ｓｉは、その結晶学的な単位格子（立方晶、空間群Ｆｄ－３ｍ）に８個のＳｉ原子を含んでいる。格子定数ａ＝０．５４３１ｎｍから換算して、単位格子体積は０．１６０２ｎｍ^{3}であり、Ｓｉ原子１個の占める体積（単位格子体積を単位格子中のＳｉ原子数で除した値）は０．０１９９ｎｍ^{3}である。ここで、Ｓｉを含む負極をＬｉを基準とした電位で１００ｍＶ以下まで充電する（Ｌｉを挿入させる）と、Ｌｉを多く含む化合物Ｌｉ$_{15}$Ｓｉ$_4$やＬｉ$_{21}$Ｓｉ$_5$が生じ、容量は約４０００ｍＡｈ／ｇに相当するが、負極の体積膨張率が極めて大きくなる。例えば、Ｌｉ$_{21}$Ｓｉ$_5$の単位格子（立方晶、空間群Ｆ－４３ｍ）には８３個のＳｉ原子が含まれている。その格子定数ａ＝１．８７５０ｎｍから換算して、単位格子体積は６．５９１８ｎｍ^{3}であり、Ｓｉ原子１個あたりの体積は０．０７９ｎｍ^{3}である。この値は単体Ｓｉの３．９５倍であり、このように充放電時の体積差が極めて大きいため、負極粒子に大きな歪みが生じ、負極粒子が微粉化するものと考えられる。その結果、負極粒子間に空間が生じ、負極粒子間の電気的接触（電子伝導ネットワーク）が分断され、電気化学的な反応に関与できない部分が増加し、充放電容量が低下するものと考えられる。

【００１０】また、特許文献２では、Ｓｉ粒子が黒鉛および非結晶質炭素中に埋設された複合体粒子を負極に用いたリチウム二次電池が開示され、充放電特性に優れたリチウム二次電池を実現している。このようにＳｉ粒子を黒鉛および非結晶質炭素と複合化することによって、Ｓｉの膨張が緩和でき、サイクル特性は向上する。しかし、およそ１０００ｍＡｈ／ｇ以上の高容量を発現するような複合体粒子では、サイクル特性は完全ではなく実用化に適するレベルに達しない。これは、上記のような高容量を発現するには、Ｓｉに多くのＬｉが挿入される

必要があるため、Ｓｉの膨張がさらに大きくなり、複合体粒子の構造が破壊されるためと考えられる。

【００１１】本発明は、上記従来の問題を解決し、高容量でかつサイクル特性に優れた非水二次電池を構成することのできる電極材料およびその製造方法、並びにその電極材料を用いた非水二次電池用負極および非水二次電池を提供するものである。

【００１２】

【課題を解決するための手段】本発明は、リチウムと合金化可能な元素を含む材料と、導電性材料とを含む複合体粒子からなる電極材料であって、前記リチウムと合金化可能な元素を含む材料の割合が、前記複合体粒子の全質量に対して３０質量％以上８０質量％以下であり、前記複合体粒子が、内部に空隙を有し、前記複合体粒子の嵩密度をＤ１（ｇ／ｃｍ^3）、前記複合体粒子の真密度をＤ２（ｇ／ｃｍ^3）、前記複合体粒子の空隙体積占有率（％）をＶｓ＝（１－１．３５×Ｄ１／Ｄ２）×１００とした場合、Ｖｓが３５％以上７０％以下である電極材料を提供する。

【００１３】また、本発明は、上記電極材料の製造方法であって、前記リチウムと合金化可能な元素を含む材料と、前記導電性材料と、樹脂とを混合して造粒することにより複合体粒子を形成する工程と、前記複合体粒子を加熱して前記樹脂を燃焼または昇華させて除去することにより、前記複合体粒子内に空隙を形成する工程とを含む電極材料の製造方法を提供する。

【００１４】また、本発明は、上記電極材料の製造方法であって、前記リチウムと合金化可能な元素を含む材料と、前記導電性材料とを溶媒中で分散させて混合物とし、前記混合物を噴霧して乾燥するスプレードライ法により造粒することにより複合体粒子を形成する工程を含む電極材料の製造方法を提供する。

【００１５】また、本発明は、上記電極材料を含む非水二次電池用負極を提供する。

【００１６】また、本発明は、上記非水二次電池用負極と、正極と、非水電解質とを備えた非水二次電池を提供する。

【００１７】

【発明の実施の形態】先ず、本発明の電極材料の実施の形態について説明する。本発明の電極材料の一形態は、リチウムと合金化可能な元素を含む材料と、導電性材料とを含む複合体粒子からなる電極材料であって、リチウムと合金化可能な元素を含む材料の割合が、複合体粒子の全質量に対して３０質量％以上８０質量％以下であり、その複合体粒子が内部に空隙を有し、複合体粒子の嵩密度をＤ１（ｇ／ｃｍ^3）、複合体粒子の真密度をＤ２（ｇ／ｃｍ^3）、複合体粒子の空隙体積占有率（％）をＶｓ＝（１－１．３５×Ｄ１／Ｄ２）×１００とした場合、Ｖｓが３５％以上７０％以下である。

【００１８】ここで、空隙体積占有率Ｖｓ＝（１－１．

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３５×Ｄ１／Ｄ２）×１００は、複合体粒子の体積に対する複合体粒子内の空隙体積の割合を意味する。すなわち、複合体粒子を真球状であると仮定すると、その球が３次元的に最密充填する場合、面心立方格子状に充填され、その充填率（％）は、下記のとおりとなる。
【００１９】
【数１】

$$(\sqrt{2}\pi/6) \times 100 = 74.05\%$$

【００２０】よって、嵩密度は最密充填に伴う粒子間の空隙と粒子内の空隙とを合わせた空隙量を反映した値となる。以上から、粒子内部の空隙は（０．７４０５・１／Ｄ１）－（１／Ｄ２）で表すことができ、空隙体積占有率はこれを粒子全体の体積（０．７４０５・１／Ｄ１）で除したものとなる。１／０．７４０５≒１．３５とすると、上式は１－１．３５×Ｄ１／Ｄ２となり、空隙体積占有率（％）はこれに１００をかけて、Ｖｓ＝（１－１．３５×Ｄ１／Ｄ２）×１００となる。

【００２１】複合体粒子の空隙体積占有率（Ｖｓ）が３５％未満であると、充電時に複合体粒子が大きく膨張してしまう。すなわち、Ｌｉイオンの挿入（充電）に伴って、リチウムと合金化可能な元素を含む材料が膨張する際に、複合体粒子内にその膨張分を吸収する隙間が足りないため、複合体粒子が大きく膨張することが避けられない。一方、Ｖｓが７０％を超えると、複合体粒子の作製そのものが困難となり、また、複合体粒子中の隙間が多くなりすぎて、リチウムと合金化可能な元素を含む材料と導電性材料との電子伝導ネットワークが構築されにくいため、充放電されにくくなる。なお、上記複合体粒子の嵩密度は、所定量の複合体粒子を容器に入れ、嵩密度測定装置を用いて、ＪＩＳ法に準拠した嵩密度測定方法（ＪＩＳ　Ｒ１６２８）から求める。また、真密度は、ヘリウムガスを用いたガス置換式の密度計から求める。

【００２２】また、リチウムと合金化可能な元素を含む材料の含有率は、複合体粒子の全質量に対して３０～８０質量％の範囲にある必要があり、特に４５～６５質量％の範囲が好ましい。３０質量％未満の場合は、１０００ｍＡｈ／ｇ程度の高容量を実現させるときに、リチウムと合金化可能な元素を含む材料の利用率が高くなりすぎて、複合体粒子の膨張が大きくなり、微粉化しやすくなる。また、８０質量％を越えると、導電性材料との接触点が少なくなるため、電子伝導ネットワークの構築が困難となる。なお、この含有率は、蛍光Ｘ線による定性・定量分析から求めることができる。

【００２３】上記複合体粒子に含まれるリチウムと合金化可能な元素を含む材料は、化合物でも元素単体（金属、半金属または半導体元素など）でもよく、また、結晶、低結晶およびアモルファスのいずれの状態でもよい。例えば、化合物としては酸化物や窒化物などが挙げられ、金属としては他の金属との合金や固溶体などが挙

6

げられ、他に金属間化合物でもよい。また、Ｓｉ、Ｇｅなどの半導体元素にＢやＰをドープしてｎ型あるいはｐ型の半導体となり電気抵抗が大きく低下したものを用いてもよい。リチウムと合金化可能な元素を含む材料は、体積膨張による内部応力の集中を避けるために球形が望ましい。また、Ｌｉと合金化可能な元素としては、Ａｇ、Ａｕ、Ｚｎ、Ｃｄ、Ａｌ、Ｇａ、Ｉｎ、Ｔｌ、Ｇｅ、Ｐｂ、Ｓｉ、Ｓｎ、Ｓｂ、Ｂｉなどの元素が好ましく用いられる。この中で、Ｓｉが最もＬｉの吸蔵量が大きく、かつ安価で環境面でも問題がないため特に好ましい。

【００２４】また、上記リチウムと合金化可能な元素を含む材料は、平均粒径が２μｍ以下の粒子であることが好ましい。複合体粒子が微粉化し難くなり、より効果的にサイクル耐久性を向上できるからである。

【００２５】本発明においては、複合体粒子が所定の空隙体積占有率を有することにより、その空隙を有効に活用し、充放電時のＬｉと合金化可能な元素を含む材料の体積膨張を吸収し、複合体粒子自体の体積膨張を抑制することができる。そのため、導電性材料としては、空隙を形成し易い繊維状またはコイル状の炭素材料および繊維状またはコイル状の銅などの金属材料から選ばれる少なくとも一つであることが好ましい。特に、繊維状炭素材料は、従来の粒子状のアセチレンブラックや人造黒鉛と比較して、柔軟性のある細い糸状であるため、接合または隣接する上記リチウムと合金化可能な元素を含む材料の膨張・収縮に効果的に追従することができ、加えて、嵩密度が大きいために、上記Ｌｉと合金化可能な元素を含む材料と多くの接合点を持つことができる。さらに、膨張・収縮に効果的に追従させるために、繊維状炭素材料は、塑性変形できるような弾性力を有するものがより好ましい。

【００２６】繊維状炭素材料としては、その繊維長と直径は特に制限されないが、平均繊維長は１μｍ以上３０μｍ以下が好ましい。この範囲内であれば、複合体粒子内の電気的な接合が良好となり、複合体粒子内に電子伝導ネットワークを構築することができ、充放電特性が向上する。また、繊維状炭素材料の直径は２μｍ以下が好ましい。この範囲内であれば、繊維状炭素材料が十分な弾性を有し、リチウムと合金化可能な元素を含む材料の充放電サイクルに伴う膨張・収縮に効果的に追従できる。

【００２７】この繊維状炭素材料は強い混練や分散処理によって粉砕されやすく、繊維状の形態をとれなくなる可能性がある。よって、複合化の際には繊維状炭素材料が粉砕されにくい条件で行うのが好ましい。

【００２８】繊維状炭素材料としては、ポリアクリロニトリル（ＰＡＮ）系炭素繊維、ピッチ系炭素繊維、気相成長炭素繊維などを用いることができる。繊維状炭素材料以外の導電性材料としては、高い電気伝導性と高い保

7

液性を有し、リチウムと合金化可能な元素を含む材料が収縮しても接触を保つことができる機能を有するアセチレンブラック、ケッチェンブラックなどのカーボンブラック、人造黒鉛、易黒鉛化炭素、難黒鉛化炭素などが好適に使用できる。

【００２９】また、上記複合体粒子は、さらに炭素を含む材料によって被覆されていることが好ましい。複合体粒子の膨張を効果的に抑制し、さらに複合体粒子間の電気的接触抵抗を下げるためである。図３に炭素を含む材料によって被覆された複合体粒子の放電時と充電時の模式断面図を示す。Ｌｉと合金化可能な元素を含む材料である例えばＳｉ粒子と、導電性材料である例えばＣとを所定の空隙とともに外殻（被覆層）で覆うことにより、複合体粒子の膨張を抑制できる。

【００３０】特に、トルエンなどの炭素と水素を含む化合物からなるガス（炭化水素系ガス）を気相中で熱分解して得られる炭素、または炭素前駆体を焼成して得られる難黒鉛化炭素（ハードカーボン）系の炭素で被覆することが好ましい。これらの炭素は電子伝導性に優れているからである。また、上記２種類の炭素を組み合わせて被覆するとより効果的である。

【００３１】炭素前駆体としては石油系、石炭系のものが使用でき、例えば、合成ピッチ、タール類、フェノール樹脂、フラン樹脂、ポリアクリロニトリル、ポリ（α－ハロゲン化アクリロニトリル）などのアクリル樹脂、ポリアミドイミド樹脂、ポリアミド樹脂、ポリイミド樹脂などが使用できる。複合体粒子との混合に際して、これらの炭素前駆体を溶解する溶媒を用いてもよい。溶媒としては、例えば、テトラヒドロフラン、アセトンなどのケトン類、メタノール、エタノールなどの各種アルコール類、ジメチルホルムアミド、ジメチルアセトアミドなどのアミド類、トルエン、キシレン、ベンゼンなどの炭化水素類などが挙げられる。混合の際に溶媒を用いた場合には、焼成前に５０～１５０℃の温度で、好ましくは減圧下で混合物を加熱することにより、溶媒を除去する。

【００３２】また、上記熱分解や焼成は７００℃以上で行うのが好ましく、８００℃以上で行うのがより好ましい。処理温度が高い方が不純物の残存が少なく、かつ導電性の高い良質な炭素が得られるからである。以上の観点から、複合体粒子を炭素で被覆する場合には、リチウムと合金化可能な元素を含む材料の融点は７００℃以上であることが好ましい。

【００３３】次に、本発明の電極材料の製造方法の実施の形態について説明する。本発明の複合体粒子の製造方法の一形態は、リチウムと合金化可能な元素を含む材料と導電性材料とを造粒することにより複合体粒子を作製するものである。その後、樹脂などの炭素前駆体と混合し、炭素前駆体を炭素化するか、あるいはＣＶＤ法（Ｃhemical Vapor Deposition

8

Ｍｅｔｈｏｄ）により炭素被覆するなどの方法によって、複合体粒子を炭素で被覆することもできる。造粒方法としては、転動造粒、圧縮造粒、焼結造粒、振動造粒、混合造粒、解砕造粒、転動流動造粒、スプレードライ法による造粒などが好適に用いられる。

【００３４】スプレードライ法による造粒は、材料と溶媒とを混合したスラリーを噴霧して乾燥することにより造粒する方法である。材料粒子を２μm以下に粉砕、分散するには溶媒中で行う方が効率的であるため、スプレードライ法による造粒は２μm以下の微粒子を複合化させるのに適している。また、スプレードライ法は粒径の制御も容易であり、造粒された粒子の形状も球形であり、さらに強混練や強分散処理を行わないため、繊維状の導電性材料を用いても、繊維形状が粉砕されるおそれが少ないため、造粒方法としては特に好ましい。スプレードライ法に用いる溶媒としては、非水系溶媒（水を含まない溶媒）を用いるのが好ましい。水系溶媒（水を含む溶媒）を用いると、リチウムと合金化可能な元素を含む材料の表面が酸化される可能性が高いからである。非水系溶媒としては、特にアルコール類が取扱性や乾燥の容易性の観点から好ましい。また、スラリーの分散にはビーズミルやボールミル、湿式のジェットミルなどが好適に使用できる。分散剤を兼ねた造粒時のバインダには、ポリビニルピロリドン（ＰＶＰ）やポリビニルアルコール（ＰＶＡ）などが好適に使用できる。造粒後に残存した分散剤やバインダは、加熱処理により炭化することができる。また、スプレードライ法による造粒の後に、その粒子をさらに他の導電性材料とともに転動造粒や転動流動造粒などを行って２段階で造粒すると、効率的に空隙が導入でき、さらに電子伝導ネットワークも効率的に構築できるため特に好ましい。

【００３５】複合体粒子中の空隙体積占有率は、混合材料の種類、平均粒径、混合割合、造粒条件などを制御することで、３５～７０％を達成できる。特に、１つの複合体粒子に含まれるリチウムと合金化可能な元素を含む材料の全表面積Ｓｓと、導電性材料の全表面積Ｓｃの比Ｓｃ／Ｓｓが０．５以上５０以下であると３５％以上の空隙体積占有率を得ることが容易となる。また、ポリエチレン（ＰＥ）やポリスチレン（ＰＳ）などの樹脂を造粒前の材料に含ませて造粒し、その後に加熱して樹脂を燃焼または昇華させて除去することにより、より効果的に複合体粒子の空隙のサイズや量をコントロールできる。

【００３６】次に、本発明の非水二次電池用負極および非水二次電池の実施の形態について説明する。本発明の非水二次電池用負極の一形態は、上記で説明した本発明の電極材料を含む負極である。

【００３７】また、上記本発明の電極材料を含む非水二次電池用負極は、非水二次電池用負極の充電開始の電位をリチウム金属に対して１．５Ｖとし、この充電開始時

の複合体粒子の体積をＶ１、複合体粒子１ｇ当たり１０００ｍＡｈの電気量の充電を行った後の複合体粒子の体積をＶ２、さらにその充電状態から複合体粒子をリチウム金属に対して１．５Ｖの電位まで放電させた後の複合体粒子の体積をＶ３とした場合に、（Ｖ２－Ｖ１）／Ｖ１×１００で求められる充電時の体積膨張率（％）を６８％以下に、かつ、（Ｖ２－Ｖ３）／（Ｖ２－Ｖ１）×１００で求められる放電時の体積収縮率（％）を８５％以上にすることができる。

【００３８】これにより、高容量でかつサイクル特性に優れた非水二次電池を構成することができる。すなわち、充電時の体積膨張率が６８％を超えた場合は、負極の厚さ方向の膨張が大きくなりすぎて、負極に歪みなどが発生したり集電体である金属箔が断裂するなどして電池構造および構成材料に対して悪影響が生じやすくなる。また、充放電サイクルに伴って、複合体粒子内部あるいは複合体粒子間の電子伝導ネットワークが断絶する可能性が高くなる。一方、放電時の体積収縮率が８５％未満の場合、すなわち、充電により膨張した複合体粒子が放電時に収縮せず、充放電における粒子の膨張および収縮の可逆性に劣る場合は、リチウムと合金化可能な元素を含む材料と導電性材料との電気的接触が不十分であることが推定され、充放電サイクル特性などに問題が生じる。

【００３９】また、上記非水二次電池用負極に用いる複合体粒子は、その比表面積が５０ｍ²／ｇ未満であることが好ましい。この範囲であれば、負極に含有されるバインダが複合体粒子の表面層に埋没しないため、複合体粒子と集電体との接着性が悪化せず、不可逆容量が増加する可能性が低い。

【００４０】また、本発明の非水二次電池の一形態は、上記で説明した本発明の非水二次電池用負極と、正極と、非水電解質とを備えた非水二次電池である。

【００４１】上記非水二次電池の充電方法は特に限定はされないが、定電流、または定電流と定電圧を組み合わせた方法で行うことが好ましい。例えば、設定電圧（Ｅ）に達するまでは、充電を一定の電流値（Ｉ）で充電する定電流充電領域と、設定電圧（Ｅ）に達した後、設定電圧（Ｅ）で定電圧充電する定電圧充電領域とを組み合わせて充電を行う方法が好ましい。これにより、効率的な充電が可能となり、最短の時間で設定した容量を引き出すことができるからである。なお、充電電流値は特に限定はされないが、１０ｍＡ／ｃｍ²以下の電流密度で行うのが好ましい。これを超えると十分な容量が得られなくなる可能性があるからである。

【００４２】また、リチウムと合金化可能な元素を含む材料に吸蔵されるＬｉ量を制限することによって非水二次電池のサイクル特性が向上する場合がある。例えば、Ｓｉは充電されてＬｉとの合金（Ｌｉ：Ｓｉ）を形成するが、ｘ≦２．６２５の範囲であるのが好ましく、ｘ＝

２．６２５を越える場合（Ｌｉ₂₁Ｓｉ₈）には膨張率が大きくなり、サイクル特性が低下するという結果が得られている。

【００４３】本発明の複合体粒子は単体でバインダと混合して負極用合剤（負極構成材の混合物）とすることができるが、さらに負極用の導電材料を導入してもよい。負極用合剤を作製する際の負極用導電材料は、構成された非水二次電池において化学変化を起こさない電子伝導性材料であれば特に制限はないが、通常、天然黒鉛（鱗状黒鉛、鱗片状黒鉛、土状黒鉛など）、人造黒鉛、アセチレンブラック、ケッチェンブラックなどのカーボンブラック、炭素繊維や、金属粉（銅、ニッケル、アルミニウム、銀などの粉末）、金属繊維あるいはポリフェニレン誘導体などの導電性高分子材料を１種、またはこれらを混合して用いることができる。

【００４４】上記負極に用いるバインダとしては、例えば、でんぷん、ポリビニルアルコール、カルボキシメチルセルロース、ヒドロキシプロピルセルロース、再生セルロース、ジアセチルセルロース、ポリビニルクロリド、ポリビニルピロリドン、ポリテトラフルオロエチレン、ポリフッ化ビニリデン、ポリエチレン、ポリプロピレン、エチレン－プロピレン－ジエンターポリマー（ＥＰＤＭ）、スルホン化ＥＰＤＭ、スチレンブタジエンゴム、ブタジエンゴム、ポリブタジエン、フッ素ゴム、ポリエチレンオキシドなどの多糖類、熱可塑性樹脂、ゴム弾性を有するポリマーなどやこれらの変成体などの１種、または２種以上を混合して用いることができる。

【００４５】上記正極には、正極材料、導電材料、バインダなどが含まれる。この正極材料としては特に限定されることなく各種のものを使用することができるが、特にＬｉₓＣｏＯ₂、ＬｉₓＮｉＯ₂、ＬｉₓＭｎＯ₂、ＬｉₓＣｏᵧＮｉ₁₋ᵧＯ₂、ＬｉₓＣｏᵧＭ₁₋ᵧＯ₂、ＬｉₓＮｉ₁₋ᵧＭᵧＯ₂、ＬｉₓＭｎ₂Ｏ₄、ＬｉₓＭｎ₂₋ᵧＭᵧＯ₄（Ｍは、Ｍｇ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉ、Ｃｕ、Ｚｎ、Ａｌ、Ｃｒのうち少なくとも１種、０≦ｘ≦１．１、　０＜ｙ＜１．０、　２．０≦ｚ≦２．２）などのＬｉ含有遷移金属酸化物が好適に用いられる。

【００４６】正極用の導電材料としては、用いる正極材料の充放電電位において化学変化を起こさない電子伝導性材料であれば特にその種類は制限されない。例えば、天然黒鉛、人造黒鉛などのグラファイト類、またはアセチレンブラック、ケッチェンブラック、チャンネルブラック、ファーネスブラック、ランプブラック、サーマルブラックなどのカーボンブラック類、または炭素繊維、金属繊維などの導電性繊維類などを単独、またはこれらを混合して使用できる。これらの導電材料の中で、人造黒鉛、アセチレンブラック、ケッチェンブラックが特に好ましい。

【００４７】正極用のバインダとしては、例えば、ポリエチレン、ポリプロピレン、ポリテトラフルオロエチレ

ン（ＰＴＦＥ）、ポリフッ化ビニリデン（ＰＶＤＦ）、スチレンブタジエンゴム、テトラフルオロエチレン－ヘキサフルオロエチレン共重合体、テトラフルオロエチレン－ヘキサフルオロプロピレン共重合体、テトラフルオロエチレン－パーフルオロアルキルビニルエーテル共重合体、フッ化ビニリデン－ヘキサフルオロプロピレン共重合体、フッ化ビニリデン－クロロトリフルオロエチレン共重合体、エチレン－テトラフルオロエチレン共重合体などを使用でき、これらの材料を単独、または混合して用いることができる。また、これらの材料の中でより好ましい材料は、ＰＶＤＦとＰＴＦＥである。

【００４８】本発明の非水二次電池に用いるリチウムイオン伝導性の非水電解質としては、一般に電解液と呼ばれる液状電解質、またはゲル状ポリマー電解質、または固体電解質のいずれも用いることができるが、液状電解質やゲル状ポリマー電解質などが好ましい。

【００４９】液状電解質は、有機溶媒と、その有機溶媒に溶解するＬｉ塩とから構成されている。有機溶媒としては、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネート、γ－ブチロラクトン、１，２－ジメトキシエタン、テトラヒドロフラン、２－メチルテトラヒドロフラン、ジメチルスルフォキシド、１，３－ジオキソラン、ホルムアミド、ジメチルホルムアミド、ジオキソラン、アセトニトリル、ニトロメタン、蟻酸メチル、酢酸メチル、燐酸トリエステル、トリメトキシメタン、ジオキソラン誘導体、スルホラン、３－メチル－２－オキサゾリジノン、プロピレンカーボネート誘導体、テトラヒドロフラン誘導体、ジエチルエーテル、１，３－プロパンスルトンなどの非プロトン性有機溶媒の少なくとも１種以上を混合した溶媒を用いることができる。また、その有機溶媒に溶解させるＬｉ塩としては、例えば、ＬｉＣｌＯ₄、ＬｉＢＦ₆、ＬｉＰＦ₆、ＬｉＣＦ₃ＳＯ₃、ＬｉＣＦ₃ＣＯ₂、ＬｉＡｓＦ₆、ＬｉＳｂＦ₆、ＬｉＢ₁₀Ｃｌ₁₀、低級脂肪族カルボン酸Ｌｉ、ＬｉＡｌＣｌ₄、ＬｉＣｌ、ＬｉＢｒ、ＬｉＩ、クロロボランＬｉ、四フェニルホウ酸Ｌｉなどの１種以上を使用できる。中でも、エチレンカーボネートまたはプロピレンカーボネートと、１，２－ジメトキシエタン、ジエチルカーボネート、メチルエチルカーボネートなどとの混合溶媒に、ＬｉＣｌＯ₄、ＬｉＢＦ₆、ＬｉＰＦ₆、ＬｉＣＦ₃ＳＯ₃などを含有させた液状電解質が好ましい。これら液状電解質を電池内に注入する量は特に限定されないが、活物質の量や電池のサイズによって必要量用いることができる。この液状電解質におけるＬｉ塩の濃度は特に限定されないが、液状電解質１リットル当たり０．２～３．０モルが好ましい。

【００５０】また、ゲル状ポリマー電解質は、上記液状電解質をゲル化剤でゲル化したものに相当する。そのゲル化剤としては、例えば、ポリエチレンオキシド、ポリアクリルニトリルなどの直鎖状ポリマーまたはそれらのコポリマー、あるいは紫外線や電子線などの活性光線の照射によりポリマー化する多官能モノマー、例えば、ペンタエリスリトールテトラアクリレート、ジトリメチロールプロパンテトラアクリレート、エトキシ化ペンタエリスリトールテトラアクリレート、ジペンタエリスリトールヒドロキシペンタアクリレート、ジペンタエリスリトールヘキサアクリレートなどの四官能以上のアクリレートおよび上記アクリレートと同様の四官能以上のメタクリレートなどが用いられる。ただし、上記モノマーを使用する場合でも、モノマー自体がそのままでゲル化剤になるのではなく、それらをポリマー化したポリマーがゲル化剤として作用する。

【００５１】上記のように多官能モノマーを用いて液状電解質をゲル化させる場合、必要であれば重合開始剤として、例えば、ベンゾイル類、ベンゾインアルキルエーテル類、ベンゾフェノン類、ベンゾイルフェニルフォスフィンオキシド類、アセトフェノン類、チオキサントン類、アントラキノン類などを使用することができ、さらに重合開始剤の増感剤としてアルキルアミン類、アミノエステルなども使用することができる。

【００５２】本発明の非水二次電池の形状としては、コイン型、ボタン型、シート型、積層型、円筒型、偏平型、角型などのほか、電気自動車などに用いる大型のものなどいずれであってもよい。

【００５３】
【実施例】以下、実施例により本発明をさらに詳しく説明する。ただし、本発明はこれらの実施例に限定されるものではない。

【００５４】（実施例１）平均粒径１μｍのＳｉ粉末と、平均繊維長５μｍで直径０．２μｍの繊維状炭素（ＣＦ：カーボンファイバー）と、平均粒径２μｍの黒鉛とを、質量比でＳｉ：ＣＦ：黒鉛＝６０：３０：１０の配合比で混合し、これらを撹拌式の転動造粒機を用いて造粒した。その結果、平均粒径１０μｍの複合体粒子が得られた。その複合体粒子の真密度（Ｄ２）は２．２０ｇ／ｃｍ³、嵩密度（Ｄ１）は０．８ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率Ｖｓは、Ｖｓ＝（１－１．３５×Ｄ１／Ｄ２）×１００の式から５１％と求まった。

【００５５】次に、得られた複合体粒子９０質量部に対し、負極用導電材料として炭素粉末５質量部と、バインダとしてＰＶＤＦ５質量部とを混合し、これらを脱水Ｎ－メチルピロリドンに分散させてスラリーを作製し、銅箔からなる負極集電体上に塗布して、乾燥し、圧延した後、直径１６ｍｍの円板状に切り取って、これを真空で２４時間乾燥させて負極とした。

【００５６】上記で得られた複合体粒子について、非水二次電池用負極の電極材料としての特性を下記の方法に

13

より試験した。

【００５７】上記負極と、対極の金属Ｌｉとを組み合わせてコイン型モデル電池を作製した。電解液には、プロピレンカーボネートとジメチルカーボネートとの混合溶媒（混合体積比１：１）に六フッ化リン酸リチウムを１ｍｏｌ／Ｌ溶解したものを用いた。負極の電位がリチウム金属基準で１．５Ｖになるまで放電した後に、一部のモデル電池を分解し、後述の方法により充電開始時の複合体粒子の体積Ｖ１を求めた。次いで、残った電池を、負極の複合体粒子を１ｇ当たり１０００ｍＡｈの電気量で充電し、この中の一部の電池から同様の方法により複合体粒子の体積Ｖ２を求めた。さらに、残りの電池を、負極の電位がリチウム金属基準で１．５Ｖになるまで放電させ、放電終了後に同様の方法により複合体粒子の体積Ｖ３を求めた。この結果から、充電時の体積膨張率〔（Ｖ２－Ｖ１）／Ｖ１×１００〕と放電時の体積収縮率〔（Ｖ２－Ｖ３）／（Ｖ２－Ｖ１）×１００〕を求めた。その結果、充電時の体積膨張率は６５％であり、放電時の体積収縮率は８５％であった。

【００５８】上記複合体粒子の体積は下記の方法で求めた。測定する負極をアルゴン雰囲気下でジメチルカーボネートにより洗浄した後、大気に触れることなく気密状態で走査型電子顕微鏡（ＳＥＭ）まで搬送し、ＳＥＭ写真から任意の粒子１００個の粒径を求め、複合体粒子の形状を球状と仮定して体積を求めた。そして、１００個の平均粒子体積を、求める複合体粒子の体積とした。

【００５９】一方、上記複合体粒子を用いたコイン型モデル電池のサイクル特性を調べた。電池の充放電方法は以下のように行った。充電は電流密度を０．５ｍＡ／ｃｍ²とし、定電流で充電を行い、充電電圧が１２０ｍＶに達した後、１／１０の電流密度になるまで定電圧で充電を行った。放電は電流密度０．５ｍＡ／ｃｍ²の定電流で行い、放電終止電圧は１．５Ｖとした。

【００６０】その結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１１００ｍＡｈであり、５０サイクル目の容量保持率〔（５０サイクル目の放電容量／２サイクル目の放電容量）×１００〕は７０％であった。

【００６１】（実施例２）平均粒径１μｍのＳｉ粉末と、平均繊維長５μｍで直径０．２μｍのＣＦと、平均粒径２μｍの黒鉛とを、質量比でＳｉ：ＣＦ：黒鉛＝６０：３０：１０の配合比で混合し、これらを撹拌式の転動造粒機を用いて造粒した。その結果、平均粒径１０μｍの複合体粒子が得られた。このようにして作製した複合体粒子のＳＥＭ写真を図１に示す。

【００６２】続いて、ベンゼンをカーボン源として、ＣＶＤ法により１０００℃で複合体粒子を炭素で被覆した。被覆した炭素量は被覆前後の複合体粒子の質量変化から求めた。その複合体粒子の組成は、質量比でＳｉ：ＣＦ：黒鉛：ＣＶＤ炭素＝５６：２８：９：７であった。得られた複合体粒子の真密度は２．２０ｇ／ｃ

14

ｍ³、嵩密度は０．８５ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率Ｖｓは、前述の計算式から４８％と求まった。次に、実施例１と同様にして負極を作製したところ、実施例１と同様にして測定した充電時の体積膨張率は５０％であり、放電時の体積収縮率は９２％であった。

【００６３】また、実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０００ｍＡｈであり、５０サイクル目の容量保持率は８５％であった。

【００６４】（実施例３）平均粒径２μｍのＳｉ粒子と、平均繊維長５μｍで直径０．２μｍのＣＦと、平均粒径２μｍの黒鉛とを、質量比でＳｉ：ＣＦ：黒鉛＝６０：３０：１０の配合比で用いた以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５６質量％であり、また、その複合体粒子の真密度は２．２０ｇ／ｃｍ³、嵩密度は０．９８ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は４０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は６２％であり、放電時の体積収縮率は８８％であった。

【００６５】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり９５０ｍＡｈであり、５０サイクル目の容量保持率は７５％であった。

【００６６】（実施例４）実施例１と同じ原料を用いて、配合比を質量比でＳｉ：ＣＦ：黒鉛＝４０：３５：２５とした以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して３７質量％であり、また、その複合体粒子の真密度は２．２０ｇ／ｃｍ³、嵩密度は０．８１ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は５０％であり、放電時の体積収縮率は９２％であった。

【００６７】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり７００ｍＡｈであり、５０サイクル目の容量保持率は９５％であった。

【００６８】（実施例５）実施例１と同じ原料を用いて、配合比を質量比でＳｉ：ＣＦ：黒鉛＝７５：１５：１０とした以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して７０質量％であり、また、その複合体粒子の真密度は２．２５ｇ／ｃｍ³、嵩密度は１．０ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は４０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は５５％であり、放電時の体積収縮率は８５％であった。

15

【００６９】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１２５０ｍＡｈであり、５０サイクル目の容量保持率は７３％であった。

【００７０】（実施例６）平均粒径１μｍのＳｉ粒子と、平均繊維長１０μｍで直径０．１μｍのＣＦと、平均粒径２μｍの黒鉛とを、質量比でＳｉ：ＣＦ：黒鉛＝６０：３０：１０の配合比で用いた以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対しては５６質量％であり、また、その複合体粒子の真密度は２．２０ｇ／ｃｍ³、嵩密度は０．７３ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５５％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４５％であり、放電時の体積収縮率は９２％であった。

【００７１】実施例１と同様にして行ったサイクル試験の結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０５０ｍＡｈであり、５０サイクル目の電極の容量保持率は８７％であった。

【００７２】（実施例７）平均粒径１μｍのＳｉ粒子と、平均繊維長１０μｍで直径０．２μｍのＣＦとを、質量比でＳｉ：ＣＦ＝６０：４０の配合比で用いた以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子をコールタールピッチでコーティングした後、１３００℃で焼成して複合体粒子の表面をハードカーボンで被覆した。

【００７３】最終的に得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５２質量％であり、また、その複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．８６ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は４５％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は３５％であり、放電時の体積収縮率は９５％であった。

【００７４】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり９５０ｍＡｈであり、５０サイクル目の電極の容量保持率は８８％であった。

【００７５】（実施例８）実施例１と同じ原料に、さらに平均粒径０．２μｍのポリスチレン粒子（ＰＳ）を加え、質量比でＳｉ：ＣＦ：黒鉛：ＰＳ＝３０：１５：５：５０の配合比で用いた以外は、実施例２と同様にして複合体粒子を作製した。用いたＰＳはＣＶＤ処理時に燃焼または昇華するため粒子内に新たな空隙が形成される。最終的に得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５６質量％であり、また、その複合体粒子の真密度は２．２０ｇ／ｃｍ³、嵩密度は０．７３ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５５％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４８％であ

16

り、放電時の体積収縮率は９０％であった。

【００７６】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり９２０ｍＡｈであり、５０サイクル目の容量保持率は８５％であった。

【００７７】（実施例９）平均粒径０．２μｍのＳｉ粒子と、平均繊維長５μｍで直径０．２μｍのＣＦと、平均粒径０．０５μｍのケッチェンブラック（ＫＢ）とを、質量比でＳｉ：ＣＦ：ＫＢ＝６０：３０：１０の配合比で用いた以外は、実施例２と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５６質量％であり、また、その複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．６８ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５６％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は５０％であり、放電時の体積収縮率は９５％であった。

【００７８】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０００ｍＡｈであり、５０サイクル目の容量保持率は８７％であった。

【００７９】（実施例１０）平均粒径０．２μｍのＳｉ粉末と、平均繊維長５μｍで直径０．２μｍのＣＦと、平均粒径０．０５μｍのＫＢと、分散剤としてのポリビニルピロリドン（ＰＶＰ）とを、質量比でＳｉ：ＣＦ：ＫＢ：ＰＶＰ＝６０：３０：１０：４の配合比でエタノール中にて混合した。この混合物を湿式のジェットミルで分散混合し、その後得られたスラリーをスプレードライ法にて造粒した。その結果、平均粒径１０μｍの造粒体が得られた。続いて、トルエンをカーボン源として、ＣＶＤ法により１０００℃で複合体粒子を炭素で被覆した。被覆した炭素量は被覆前後の複合体粒子の質量変化から求めた。その複合体粒子の組成は、質量比でＳｉ：ＣＦ：ＫＢ：ＣＶＤ炭素＝５０：２５：８：１７であった。得られた複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．６８ｇ／ｃｍ³であった。従って、空隙体積占有率は５８％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４８％であり、放電時の体積収縮率は９５％であった。

【００８０】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０００ｍＡｈであり、５０サイクル目の容量保持率は９０％であった。

【００８１】（実施例１１）平均粒径０．２μｍのＳｉ粉末と、平均粒径０．０５μｍのＫＢと、分散剤としてのＰＶＰとを、質量比でＳｉ：ＫＢ：ＰＶＰ＝７０：３０：３の配合比でエタノール中にて混合した。この混合物を湿式のジェットミルで分散混合し、その後得られたスラリーをスプレードライ法にて造粒した。その結果、平均粒径３μｍの造粒体が得られた。得られた造粒体

17

（Ｓｉ／ＫＢ造粒体）と、平均繊維長５μｍで直径０．２μｍのＣＦとを、質量比でＳｉ／ＫＢ造粒体：ＣＦ＝８５：１５の配合比で混合し、その混合体を転動流動法にて造粒した。その結果、平均粒径１５μｍの複合体粒子が得られた。続いて、トルエンをカーボン源として、ＣＶＤ法により１０００℃で複合体粒子を炭素で被覆した。被覆した炭素量は被覆前後の複合体粒子の質量変化から求めた。その複合体粒子の組成は、質量比でＳｉ：ＣＦ：ＫＢ：ＣＶＤ炭素＝５０：１０：２５：１５であった。得られた複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．６５ｇ／ｃｍ³であった。従って、空隙体積占有率は６０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４７％であり、放電時の体積収縮率は９５％であった。

【００８２】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０００ｍＡｈであり、５０サイクル目の容量保持率は９２％であった。

【００８３】（実施例１２）平均粒径１．０μｍのＳｉ粉末と、平均粒径０．０５μｍのＫＢと、分散剤のＰＶＰとを、質量比でＳｉ：ＫＢ：ＰＶＰ＝７０：３０：３の配合比でエタノール中にて混合した。この混合物を湿式のジェットミルで分散混合し、その後得られたスラリーをスプレードライ法にて造粒した。その結果、平均粒径５μｍの造粒体が得られた。続いて、トルエンをカーボン源として、ＣＶＤ法により１０００℃で造粒体を炭素で被覆した。得られた複合体粒子をさらにコールタールピッチでコーティングした後、１３００℃で焼成して複合体粒子の表面をハードカーボンで被覆した。

【００８４】このようにして作製した複合体粒子のＳＥＭ写真を図２に示す。最終的に得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して４７質量％であり、また、その複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．７８ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４０％であり、放電時の体積収縮率は９５％であった。

【００８５】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり９２０ｍＡｈであり、５０サイクル目の容量保持率は９３％であった。

【００８６】（実施例１３）平均粒径１．０μｍのＳｉ粉末と、平均粒径０．０５μｍのＫＢと、分散剤のＰＶＰとを、質量比でＳｉ：ＫＢ：ＰＶＰ＝６０：４０：４の配合比でエタノール中にて混合した。この混合物を湿式のジェットミルで分散混合し、その後得られたスラリーをスプレードライ法にて造粒した。その結果、平均粒径５μｍの造粒体が得られた。続いて、カーボン源なしに１０００℃で造粒体を焼成した。最終的に得られた複

18

合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５６質量％であり、また、その複合体粒子の真密度は２．１０ｇ／ｃｍ³、嵩密度は０．７５ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５２％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は５５％であり、放電時の体積収縮率は８５％であった。

【００８７】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１０５０ｍＡｈであり、５０サイクル目の電極の容量保持率は８０％であった。

【００８８】（実施例１４）平均粒径１．０μｍのＳｉ／Ｓｉ₂Ｎｉ複合体粉末と、平均粒径０．０５μｍのＫＢと、分散剤のＰＶＰとを、質量比でＳｉ：ＫＢ：ＰＶＰ＝８５：１５：１の配合比でエタノール中にて混合した。この混合物を湿式のジェットミルで分散混合し、その後得られたスラリーをスプレードライ法にて造粒した。その結果、平均粒径７μｍの造粒体が得られた。続いて、トルエンをカーボン源として、ＣＶＤ法により８５０℃で造粒体を炭素で被覆した。最終的に得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して４０質量％であり、また、その複合体粒子の真密度は３．１０ｇ／ｃｍ³、嵩密度は１．１５ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は５０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は４０％であり、放電時の体積収縮率は９３％であった。

【００８９】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり８００ｍＡｈであり、５０サイクル目の容量保持率は９５％であった。

【００９０】（比較例１）平均粒径１μｍのＳｉ粉末と、平均粒径２μｍの黒鉛とを、質量比でＳｉ：黒鉛＝６０：４０の配合比で用いた以外は、実施例１と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して５６質量％であり、また、その複合体粒子の真密度は２．２０ｇ／ｃｍ³、嵩密度は１．１４ｇ／ｃｍ³であった。従って、この複合体粒子の空隙体積占有率は３０％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は１００％であり、放電時の体積収縮率は７７％であった。

【００９１】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり８４０ｍＡｈであったが、５０サイクル目の容量保持率は４０％であり、大幅な容量低下が認められた。

【００９２】（比較例２）平均粒径１μｍのＳｉ粉末と、平均粒径２μｍの黒鉛とを、質量比でＳｉ：黒鉛＝９０：１０の配合比で用いた以外は実施例１と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含

19

有率は、複合体粒子の全質量に対して８４質量％であり、また、その複合体粒子の真密度は２．２０ｇ／cm³、嵩密度は１．１０ｇ／cm³であった。従って、この複合体粒子の空隙体積占有率は３２％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は１１０％であり、放電時の体積収縮率は７０％であった。

【００９３】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり１４００ｍＡｈであり、５０サイクル目の容量保持率は１０％であった。

【００９４】（比較例３）平均粒径１μｍのＳｉ粉末と、平均粒径２μｍの黒鉛とを、質量比でＳｉ：黒鉛＝２５：７５の配合比で用いた以外は、実施例１と同様にして複合体粒子を作製した。得られた複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して２０質量％であり、また、その複合体粒子の真密度は２．２０ｇ／cm³、嵩密度は１．１７ｇ／cm³であった。従って、この複合体粒子の空隙体積占有率は２８％と求まった。また、実施例１と同様にして測定した充電時の体積膨張率は７５％であり、放電時の体積収縮率は８３％と求まった。

【００９５】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり５００ｍＡｈであり、５０サイクル目の容量保持率は５０％であった。

【００９６】（参考例１）コールタールピッチのテトラヒドロフラン（ＴＨＦ）溶液にテトラメトキシシラン（ＴＭＯＳ）を溶解した。この溶液に平均粒径５μｍの黒鉛を添加して、還流しながら攪拌・混合した。それぞ

20

れの配合比は質量比でＴＨＦ：コールタールピッチ：ＴＭＯＳ：黒鉛＝１０：１：１：３である。次いで、ＴＨＦを真空乾燥して除去した。得られた粉末を窒素気流中、１０００℃でコールタールピッチおよびＴＭＯＳを分解・炭素化して、珪素を含有する黒鉛および非晶質炭素からなる複合体粒子を得た。この複合体粒子のＳｉ含有率は、複合体粒子の全質量に対して６質量％であり、その複合体粒子の空隙体積占有率は１２％であった。また、実施例１と同様にして測定した充電時の体積膨張率は３０％であり、放電時の体積収縮率は８０％であった。

【００９７】実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり４００ｍＡｈであり、５０サイクル目の容量保持率は７０％であった。

【００９８】（参考例２）平均粒径２μｍのＳｉ粒子と、平均繊維長５μｍで直径０．２μｍのＣＦとを、質量比でＳｉ：ＣＦ＝６０：４０の配合比で乳鉢により混合して、電極材料とした。この電極材料は、ＳｉとＣＦとが単に混合されているのみで、複合体は形成されなかった。この電極材料を用いて実施例１と同様にして負極を作製した。

【００９９】また、実施例１と同様にしてサイクル試験を行った結果、２サイクル目の放電容量は複合体粒子１ｇ当たり６５０ｍＡｈであり、５０サイクル目の放電容量はほとんど０ｍＡｈ／ｇであった。

【０１００】以上の結果を表１に示した。

【０１０１】

【表１】

	空隙体積占有率Vs（％）	充電時の体積膨張率（％）	放電時の体積収縮率（％）	2サイクル目の放電容量（mAh/g）	50サイクル目容量保持率（％）
実施例1	51	65	85	1100	70
実施例2	48	50	92	1000	85
実施例3	40	62	88	950	75
実施例4	50	50	92	700	95
実施例5	40	65	85	1250	73
実施例6	55	45	92	1050	87
実施例7	45	35	95	950	88
実施例8	55	48	90	920	85
実施例9	56	50	95	1000	87
実施例10	58	48	95	1000	90
実施例11	60	47	95	1000	92
実施例12	50	40	95	920	93
実施例13	52	55	85	1050	80
実施例14	50	40	93	800	95
比較例1	30	100	77	840	40
比較例2	32	110	70	1400	10
比較例3	28	75	83	500	50
参考例1	12	30	80	400	70
参考例2	-	-	-	650	0

【０１０２】表１から明らかなように、実施例１～１４の複合体粒子は、充電時における粒子の膨張が少なく、かつ放電時において可逆的に収縮できることが分かる。また、大きな放電容量を示し、充放電サイクルを繰り返しても容量低下が少なくサイクル特性にも優れていた。一方、空隙体積占有率が小さい比較例１～３は、充電時

21

22

の膨張が大きく、可逆性に劣り、充放電サイクル後の容量保持率も著しく低くなった。

【０１０３】なお、参考例１は特許文献２を参考にした例であり、参考例２は複合体粒子を形成させていない例である。

【０１０４】

【発明の効果】以上説明したように本発明は、電極材料の膨張を抑えることにより、高容量でかつサイクル特性に優れた非水二次電池を構成することができる。

【図面の簡単な説明】

【図１】　本発明の実施例２における複合体粒子のＳＥＭ写真である。

【図２】　本発明の実施例１２における複合体粒子のＳＥＭ写真である。

【図３】　炭素を含む材料によって被覆された複合体粒子の放電時と充電時の模式断面図である。

【図１】

【図２】

10
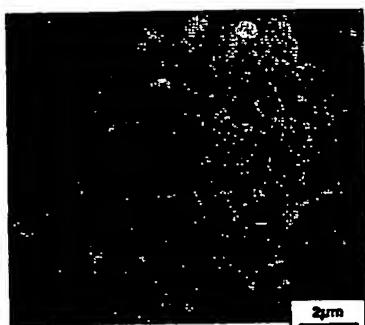
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【図３】
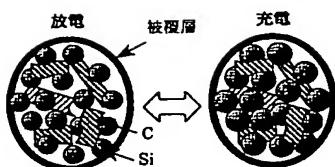
30

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